



Review Paper

Second-generation bioethanol from industrial wood waste of South American species

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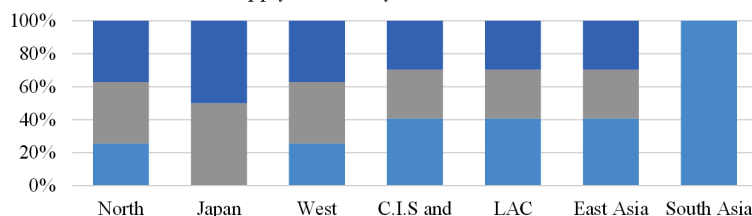
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HIGHLIGHTS

- Second generation bioethanol is a viable option to valorize the residues of the South America forest industry.
- Eucalyptus and pines are the most important woody raw materials in the region.
- Autohydrolysis and alkaline treatments are effective options to pretreat Eucalyptus.
- Novel and complex treatments or treatment combinations are recommended for pine-based ethanol production.
- Raw material price plays a key role in the cost distribution of cellulosic bioethanol.

GRAPHICAL ABSTRACT

Potential supply of forestry residues and wastes in 2050



	North America	Japan	West Europe	C.I.S and Baltic	LAC America	East Asia	South Asia
Wood harvest residues (t y ⁻¹)	1.11 10 ⁸	n.d.	5.26 10 ⁷	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	5.26 10 ⁷
Wood process residues (t y ⁻¹)	2.11 10 ⁸	5.26 10 ⁸	1.11 10 ⁸	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	n.d.
Wood wastes (t y ⁻¹)	2.11 10 ⁸	5.26 10 ⁸	1.11 10 ⁸	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	n.d.

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ABSTRACT

There is a global interest in replacing fossil fuels with renewable sources of energy. The present review evaluates the significance of South-American wood industrial wastes for bioethanol production. Four countries have been chosen for this review, i.e., Argentina, Brazil, Chile, and Uruguay, based on their current or potential forestry industry. It should be noted that although Brazil has a global bioethanol market share of 25%, its production is mainly first-generation bioethanol from sugarcane. The situation in the other countries is even worse, in spite of the fact that they have regulatory frameworks in place already allowing the substitution of a percentage of gasoline by ethanol. Pines and eucalyptus are the usually forested plants in these countries, and their industrial wastes, as chips and sawdust, could serve as promising raw materials to produce second-generation bioethanol in the context of a forest biorefinery. The process to convert woody biomass involves three stages: pretreatment, enzymatic saccharification, and fermentation. The operational conditions of the pretreatment method used are generally defined according to the physical and chemical characteristics of the raw materials and subsequently determine the characteristics of the treated substrates. This article also reviews and discusses the available pretreatment technologies for eucalyptus and pines applicable to South-American industrial wood wastes, their enzymatic hydrolysis yields, and the feasibility of implementing such processes in the mentioned countries in the frame of a biorefinery.

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Contents

1. Introduction	655
2. Forestry and wood waste in South America	655
3. Pine and eucalyptus pretreatments for bioethanol production	657
4. Technical and economic aspects of bioethanol production	663
5. Conclusions	664
References	664

1. Introduction

The global use and production of biofuels have grown significantly in the last decade. The prominence of biofuels is evidenced by the increase of their production from 46 million L in 2006 to 118 million L in 2013 (Zaman et al., 2016). At commercial scale, ethanol is combined with gasoline, and biodiesel is blended with diesel. The main interest in biofuel production is attributed to the reductions achieved in the emission of greenhouse gasses (GHG) produced by fossil fuels. Nowadays, about 60% of the global bioethanol production is based on sugarcane while the rest is obtained mainly from corn and other crops. However, the use of edible crops for biofuels production has led to significant pressure on arable land originally used for the production of food crops and hence, investigation of other carbohydrate sources of no food/feed value is a necessity (Solomon and Bailis, 2014; Cremonese et al., 2015).

The development of bioethanol production responds more to social mandates rather than to economic issues. In fact, national and international policies including subsidies and tax exemptions, as well as biofuel blending mandate strongly encourage the production of biofuels (Laaksonen-Craig, 2008; Willem van Gelder et al., 2012; Cremonese et al., 2015). Without regulations, generally propped up by local producers or NGOs, bioethanol production would not have stood a chance to develop due to the fierce competition with the oil industry. For example, some of the recent regulations about biofuels in the European Union (i.e., Renewable Energy Directive 2009/28/EC, Fuel Quality Directive 2009/30/EC, and Directive to reduce indirect land use change for biofuels and bioliquids (EU)2015/1513), as well as in the United States (i.e., Energy Policy Act (EPAct) 2005 and 2013 Cellulosic Biofuel Standard, Final Rule, U.S. EPA, Vol. 79, No. 85, May 2, 2014) have targeted increased inclusion percentage of renewable fuels in gasoline with a focus on the use of cellulosic and lignocellulosic materials as raw materials (EBTP, 2009; Duffield et al., 2015). The United States has set forth plans to produce 60 billion L of second-generation biofuel, i.e., about 20% of its liquid transportation fuel, by the year 2022. These biofuel policies have driven the second-generation biofuel development (Eisentraut, 2010; Balan, 2014). North America, especially the United States, has been an outstanding leader in cellulosic ethanol production (Griffin et al., 2016). Extensive information about biofuels policies and regulations can be found in the literature (Solomon et al., 2007; Sorda et al., 2010; Solomon and Bailis, 2014).

In Brazil, Proalcool (National Ethanol Program) Decree n. 76.593, 1975, first mandated the addition of ethanol to gasoline for use in motor vehicles, initiating a great expansion of the bioethanol industry in the country. Later, Law 10.464 / 02, 2002, requested for a mandatory blend of between 20 and 25% (Cassuto and Gueiros, 2012). Pilot plants of second-generation bioethanol are already operating in Brazil but the financing needed for commercial plants of such is around of USD 125-250 million (Eisentraut, 2010). In Argentina, the Law 26.093, Regime of Regulation and Promotion for the Sustainable Production and Use of Biofuels, 2006, stipulated 5% fuel bioethanol in the gasoline mix (Diputados, Senado y Cámara de Argentina, 2006). In line with that, Argentina produced around 350,000 m³ of first-generation bioethanol from sugarcane and corn in the year 2010 (García et al., 2011) but the mandate was never fulfilled (Biofuels-Digest, 2016). Nevertheless, recent regulations have raised the proportion of bioethanol in gasoline to 10% (Lemos and Mesquita, 2016). Chile has also announced the intention of developing second-generation biofuels but it lacks available biomass resources (Eisentraut, 2010).

The global production of bioethanol in the year 2015 was 90 billion L (Araújo, 2016) out of which the United States and Brazil accounted for more than 70% (Achinas and Euverink, 2016). The liquid biofuels production also resulted for about 1.8 million jobs created worldwide in the year 2014, 47% of which took place in Brazil (Araújo, 2016). Latin America and the Caribbean reached a 27% of the worldwide biofuel production in the year 2012, mostly in

the form of bioethanol and biodiesel (Solomon and Bailis, 2014). Brazil is the largest producer of ethanol in this region since the year 1960 and one of the main producers on a global scale. The market for first-generation ethanol is already established in Brazil, Colombia, and Argentina whilst it is in its developing stages in Paraguay and Bolivia as well (Janssen and Rutz, 2011).

The high volumes of wood industrialized in South American countries coupled with their intention to turn to renewable energies, make the second-generation bioethanol production a viable option to valorize the residues of the forest industry. It should be noted that the forest industry is in general relying increasingly on forests located in South America, Africa, and Asia (Toppinen et al., 2010). For example, pulp trade increased by 3% in 2015 due to the startup of new pulp mills in Brazil and Uruguay (FAO, 2015). Uruguay has encouraged forestry in the last decades, and consequently, the new forest sector has grown rapidly, attracting foreign investments due to the attractive cost-benefit ratios (Olmos and Siry, 2009). The main forest cultures in South America are pines and eucalyptus. These species are globally considered as good raw materials for papermaking and wood products and are mainly industrialized in Brazil, Chile, Uruguay, and Argentina (FAO, 2006).

The use of the lignocellulosic biomass is considered as a sustainable pathway for biofuels production as substitution for fossil fuels. Life cycle assessment studies evaluating the environmental implications of the production of ethanol from fast-growing wood crops in comparison with conventional gasoline have shown reductions in almost all impact categories under assessment when shifting to ethanol-based fuels (González and García, 2015). Another advantage of or second-generation ethanol (cellulosic bioethanol) over the technologically mature first-generation ethanol is the ability to use different types of lignocellulosic materials as a source of glucose. In this context, lignocellulosic materials are being intensely studied as feedstocks for bioethanol production, while focusing on improving the technological processes involved in order to reduce the production cost of fermentable sugars and their fermentation to ethanol (Alvira et al., 2010; Zhu et al., 2010; Zhu and Pan, 2010; Solomon and Bailis, 2014; Achinas and Euverink, 2016; Araújo, 2016; Zabad et al., 2017). However, among sixteen commercial-scale cellulosic ethanol projects using sugar platform in the world in the year 2012, only one has been based on wood as raw material (Araújo, 2016).

The present manuscript briefly reviews forestry and wood industry in South America and the potentials for biofuels and particularly bioethanol production. It also presents a short description of the main regional forest resources and their characteristics, including the availability of wood residues that could be potential sources for bioethanol production. Subsequently, available pretreatment technologies and their enzymatic hydrolysis (EH) yield for the main feedstocks of the South-American wood industry, i.e., eucalyptus and pines wood wastes were discussed. Finally, the feasibility of implementing relevant processes in the frame of a biorefinery for Argentina, Brazil, Chile, and Uruguay was presented.

2. Forestry and wood wastes in South America

Forest plantations in South America consist almost exclusively of fast-growing exotic species. For example, *Eucalyptus* and *Pinus* in Brazil have rotation lengths of 8-10 and 16-25 years and mean annual increments of 18-20 and 15-25m³ ha⁻¹ yr⁻¹, respectively (FAO, 2001). Much progress has been made in the improvement of the yield and in the silviculture of fast-growing species, since in Argentina, for example, the growth is almost two folds that of two decades ago. In addition to the geographical advantages, this is due to the permanent development of silvicultural techniques oriented to improve the productivity and sustainability of the plantations.

Plantations have been observed in recent times due to their alleged negative effects on water resources, soil, and biodiversity. Hence, efforts have been intensified to design plantations adapted to specific conditions of each region, and site, with the purpose of minimizing or totally avoiding such effects, and on the contrary to increase the production of environmental services such as watershed regulation, carbon capture, and soil stabilization (Idígoras, 2016).

The most relevant species and the most suitable lignocellulosic wastes potentially available as feedstock for the production of ethanol in South America are shown in Table 1. The advantages of wood wastes compared with

agro-industrial wastes are related to the harvesting, storage, and transportation. Wood wastes are in general unexploited resources with great potential for ethanol production (220-285 L/ton of wood). They have low ash content and their transport cost is low because of their high density, as compared with agro-industrial wastes (Zabed et al., 2017).

Most wastes from sawmills in Argentina and Brazil are scarcely utilized and are usually burned for energy production. In Brazil and based on the data recorded in the year 2007, about 30% of the forestry processing residues (5,500,000 tons of dry matter per year) were unused (Kline et al., 2008). The projections of the wastes and biomass associated with current

Table 1. Forest resources and lignocellulosic wastes available as feedstock for the production of 2nd generation bioethanol in South America.

Country	Region	Harvesting area (ha)	Plant type or waste	Area (%)	Amount of waste (ton/y)	Ethanol production potential	Reference
Argentina	Total country	648,000	<i>Pinus elliottii</i> and <i>Pinus taeda</i>	54	-	-	Senasa (2014)
		384,000	<i>Eucalyptos</i>	32	-	-	
		108,000	<i>Salicaceae</i> (%)	9	-	-	
		60,000	Others	5	-	-	
Argentina	Misiones	200,000	<i>Pinus elliottii</i> and <i>Pinus taeda</i>	-	-	-	Area and Vallejos (2012) PROBIOMASA (2012) Stoffel (2016)
			Total wood waste	-	2,101,494	-	
			Wood waste available	-	416,096	-	
Argentina	Mesopotamian region	200,000	<i>E. grandis</i> , <i>E. saligna</i> , and <i>E. dunni</i>	52% with respect to total	-	-	Carpineti (1995)
			Eucalyptus wastes	-	-	400,000	Ruz et al. (2014)
Argentina	Delta region and south of Argentina	-	<i>Salicaceae</i>	9	-	-	Senasa (2014)
Argentina	Córdoba	-	Corncocks	-	100,000	-	Ruz et al. (2014)
Argentina	San Juan and Mendoza	-	Vineyard pruning	-	235,000	-	Ruz et al. (2014)
Argentina	Tucumán	-	Sugarcane straw	-	260,000	-	Ruz et al. (2014)
			Sugarcane bagasse	-	200,000	-	
Brazil	-	-	<i>E. grandis</i> and <i>E. urophylla</i>	-	-	-	Castro et al. (2016)
Brazil	North, south east, and south of Brazil	-	Forestry waste	-	4,300,000	-	Kline et al. (2008)
	South east and south of Brazil	-	Sawdust	-	1,185,000	-	
Brazil	Alagoas and Pernambuco, Goiás, Mato Grosso do Sul, Sao Paulo, Minas Gerais, Paraná	-	Sugarcane straw and bagasse	-	500,000 to 2,000,000 per season	-	Ruz et al. (2014)
Chile	The whole country	2.872 million	<i>Pinus radiata</i>	68	-	-	CONAF (2011)
			<i>Eucalyptus</i>	23	-	-	-
			<i>Pinus radiata</i> waste (cellulosic industry)	-	2,234,000	-	CNE/GTZ (2008)
			<i>Eucalyptus</i> waste (cellulosic industry)	-	-	-	-
			-	-	536,000	-	CNE/GTZ (2008)
Chile	Araucania region	-	Wheat straw	-	500,000	-	Ruz et al. (2014)
Chile	O'Higgins region	-	Corncocks	-	500,000	-	Ruz et al. (2014)
Chile	Coquimbo, Valparaíso, Metropolitana, O'Higgins, and Maule	-	Apple and vineyard pruning	-	150,000 to 280,000	-	Ruz et al. (2014)
Uruguay	Total Departments of Paysandú and Rio Negro Departments Paysandú and Rivera	-	-	99%	-	-	Boscana and Boragno (2016)
			<i>Eucalyptus</i>	58% of the total	-	-	Boscana and Boragno (2016)
			<i>E. dunni</i> ,	-	-	-	-
			<i>E. grandis</i> ,	29% of the total	-	-	Boscana and Boragno (2016)
			Total <i>Eucalyptus</i> forestry residues	-	90,000 to 140,000	-	Ruz et al. (2014)
Uruguay	Departments of Tacuarembó and Rivera	-	<i>Pinus (P. taeda)</i> ,	-	-	-	Boscana and Boragno (2016)
Paraguay	Guaira	-	Sugarcane bagasse	-	54,000	-	Ruz et al. (2014)

forestry activities which are potentially available for bioethanol production between the years 2017 and 2027 in Brazil and Argentina could stand at 7,800,000 and 500,000 of metric tons, respectively.

Biomass wastes derived from the lumber industry (sawdust, bark, and harvesting residues) can reach 1.8 million of m³ in Chile between 2019 and 2021. These wastes are used as industrial fuel to generate heat and electricity (Berg and Segura, 2016). A current ongoing initiative is the consortium BIOENERCEL S.A., which was created to develop technologies and human resources for the conversion of lignocellulosic biomass to ethanol and biodiesel (García et al., 2011).

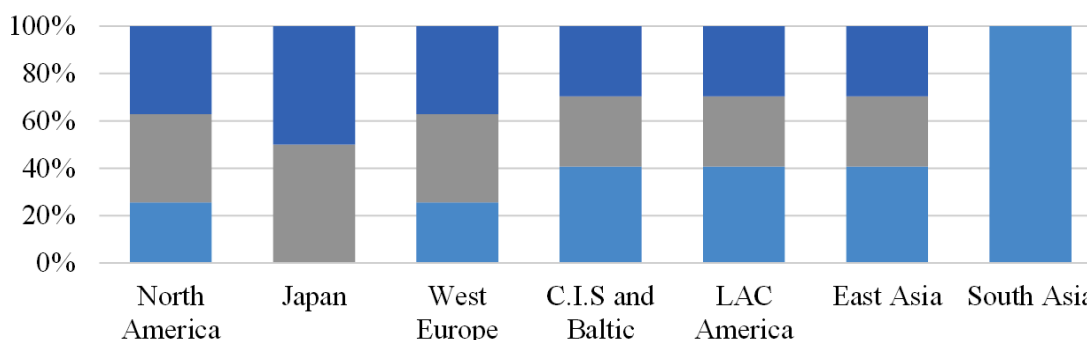
The estimation of the available volumes of current and potential lignocellulosic materials from wood wastes is tough to quantify due to the social and environmental complexity of the scenarios. However, the potential growth of the forest surplus in the year 2050, in a scenario of average plantations and demands, is estimated at 6.4 Gm³ (74 EJ yr⁻¹) where 40% is expected to end up as wastes. Figure 1 shows the proportion of forest residues and wastes potentially available, estimated from a study on the global bio-energy potentials towards 2050.

Cellulose, hemicelluloses, and lignin are the main components of wood in all trees. Lignin is formed by random copolymers deriving from unsaturated alcohol derivatives of phenyl-propane, having several functional groups as methoxyl, phenyl hydroxyl, benzyl alcohol, and carbonyl groups. Hemicelluloses are composed mostly of glucuronoxylan, glucomannan, galactoglucomannans, arabinoxylans, and glucuronoarabinoxylans in hardwoods and gramineous plants, whereas they are formed mainly of galactoglucomannans, arabinoglucuronoxylan, and arabinogalactan in softwoods. Cellulose is formed by linear polymers of β (1-4) D-glucopyranosyl units, mostly aggregate in crystalline, highly ordered structural entities. Hardwoods and softwoods also have minor but varying amounts of extractives as fats, waxes, alkaloids, proteins, gums, resins, starches, and ash (Vallejos et al., 2017). Lignin is not bound directly to cellulose, but it is covalently bound to hemicelluloses, which is in direct relation with the swelling capacity of wood (Salmén and Burgert, 2009).

A comparison of the chemical composition of regional (South American) woods is shown in Table 2.

The data presented in the table reveal the great variations in chemical

Potential supply of forestry residues and wastes in 2050



	North America	Japan	West Europe	C.I.S and Baltic	LAC	East Asia	South Asia
Wood harvest residues (t y ⁻¹)	1.11 10 ⁸	n.d.	5.26 10 ⁷	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	5.26 10 ⁷
Wood process residues (t y ⁻¹)	2.11 10 ⁸	5.26 10 ⁸	1.11 10 ⁸	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	n.d.
Wood wastes (t y ⁻¹)	2.11 10 ⁸	5.26 10 ⁸	1.11 10 ⁸	5.26 10 ⁷	5.26 10 ⁷	1.11 10 ⁸	n.d.

Fig.1. Proportion of forest residues and wastes potentially available, estimated from a study of the global bio-energy potentials to 2050 (adapted from Smeets et al., 2007). * n.d.: not defined.

Wood harvest residues are twigs, branches, and stumps. Industrial process residues are residues generated during the processing of wood into final products. Most wood processing residues are sawdust and wood chips. Wood waste is discarded wood products, such as waste paper and demolition wood. The estimated bioenergy potential of wood wastes based on their energy content on dry basis ranges from 17 to 21 MJ/kg are (average 19 MJ/kg) and accordingly, bioenergy production potentials at global scale will be: wood harvest residues 8 EJ yr⁻¹, wood process residues 11 EJ yr⁻¹, and wood waste 11 EJ yr⁻¹, 1 EJ = 10¹⁸ J (Smeets et al., 2007; González and González, 2015).

The wood of the genus *Eucalyptus* has a similar structure, indistinctly of the species. They have libriform fibers for mechanical support (between 40 and 80% of the tissue), fiber-tracheids, and vascentric tracheids for both transport and support, and vessel cells with tubular form elements that are interconnected to form long vessels for liquids transport. Despite this, there is a great variation in density and durability among species. For example, the specific gravity of *E. grandis* varies between 0.48 and 0.64, whereas that of *E. globulus* is 0.68-0.82 and for *E. camaldulensis* (industrialized wood) is 0.67-0.87 (Meier, 2015).

On the contrary, ninety percent of the wood structure of conifers is formed by a single kind of longitudinal cells (tracheids) which perform both liquid transport and support (Area and Popa, 2014). Loblolly pine has greater growth rates and is more suitable for the pulp industry and some uses of wood whereas slash pine is a rustic species which produces resin, sometimes commercialized as a by-product. Both loblolly and slash pines are harder, denser (specific gravities: 0.41-0.51 *P. radiata*; 0.47-0.57 *P. taeda*; 0.54-0.66 *P. elliotii*), and possess better strength-to-weight ratio than radiata pine (Meier, 2015).

composition due to the different species and ages of the trees. For example, old trees of *E. camaldulensis* (red eucalyptus), widely used in sawmills, show a composition totally different from *E. grandis* used for pulp manufacture, proving that the processes of conversion of raw materials into sugars for bioethanol production must be optimized in each case.

3. Pine and eucalyptus pretreatments for bioethanol production

A pretreatment is essential to make cellulose more accessible to the enzymatic attack for the production of second generation bioethanol. The requirements that an effective pretreatment should meet are (Bengochea et al., 2012):

- Reduction of the crystallinity of cellulose.
- Elimination of acetyl groups from hemicelluloses.
- Elimination of the bonds between hemicelluloses and lignin, with the consequent separation of lignin.
- Increase in the surface area of the material.
- Obtaining high yield of sugars (hexoses and pentoses).
- Minimal formation of toxic degradation products to avoid or simplify the detoxification stage.
- Low energy consumption and investment cost.
- Use of cheap and easily recoverable reagents.
- Minimal degradation of hemicellulosic sugars.

The most promising strategy is to integrate ethanol production within a biorefinery scheme in which lignin, hemicelluloses, and extractives from the lignocellulosic biomass would be converted into high-value coproducts.

Table 2.
Comparative chemical composition of regional *Pinus* and *Eucalyptus*.

Component (%)	<i>P. elliotti</i> * (1)	<i>P. radiata</i> ** (2)	<i>P. taeda</i> * (3)	<i>E. camaldulensis</i> * (4)	<i>E. grandis</i> ** (5)	<i>E. viminalis</i> ** (6)	<i>E. globulus</i> *(7)
Cellulose	46.6	41.2	41.0	41.8	51.1	47.71	43.8
Hemicelluloses	22.0	26.0	10.5	12.11	19.2	23.08	20.7
Lignin	27.2	27.8	31.5	31.3	26.2	25.00	27.1
Extractives (organic solvent)	4.60	1.90	6.00	6.59	1.20	3.72	1.80
Ashes	-	-	0.40	0.59	0.20	0.49	-

* Old trees; ** 8-9 years-old trees; (1) Stoffel et al. (2014); (2) Estimated from Reyes et al. (2013); (3) Mattos et al. (2016); (4) Rangel et al. (2016); (5) Estimated from Fardim and Durán (2004); (6) Estimated from Ramos et al. (2000); (7) Estimated from Reina and Resquin (2011).

This would assist with compensating for the costs associated with pretreatment and enzymes used for the hydrolysis of cellulose. The biorefinery thereby extends the concept of pretreatment to a fractionation of the material, obtaining fractions as pure as possible for their use and transformation into high-value products.

The most studied pretreatments and their effects are:

- Mechanical treatments (milling, extrusion, thermomechanical, refining): decrease the size of the particles to increase the surface area making them more accessible to enzymes.
- Hot water (auto-hydrolysis): liquid hot water treatment leads to deacetylation of xylans, acidifying the solution with acetic acid which catalyzes the hydrolysis of hemicelluloses, mostly in case of hardwood and grasses.
- Dilute acid: hydrolyzes hemicelluloses and the less crystalline cellulose into sugars, generating also degradation products.
- Steam explosion: the injection of high-pressure saturated steam followed by a sudden decompression to atmospheric pressure produces the separation of fibers and the depolymerisation and breaking of lignin-carbohydrates bonds, promoting the extraction of hemicelluloses.
- Supercritical CO₂: leads to impregnation and is effective to extract substances of low polarity. It also acts as a mildly acidic extraction and saccharification system for hemicelluloses.
- Organosolv delignification (catalyzed with acids or alkalis): catalysts break the internal bonds between lignin and hemicelluloses and the solvent promotes the extraction of lignin.
- Sulfite delignification in acid media: extracts lignin from wood in the form of lignosulfonates and also hemicelluloses, depending on the strength of the liquor and the severity of the conditions used.
- Alkaline delignification (kraft process, oxygen delignification): leads to the swelling of the fibers and extracts mostly lignin by splitting of lignin-carbohydrates bonds and lignin hydrolysis.
- Ultrasonic irradiation: enhances chemical treatments.
- Biological treatment by microorganisms or enzymes: produce wood degradation components, increasing porosity.
- Ionic liquids: result in biomass dissolution and promote structural changes in the regenerated biomass by reduction of cellulose crystallinity and lignin content.

A detailed description of all these processes, including their mechanisms, characteristics, advantages, and disadvantages, can be found in Brodin et al. (2017). Since the different lignocellulosic materials have different physicochemical characteristics, it is necessary to adopt appropriate pretreatment/s for each one.

Softwoods have been recognized as a highly recalcitrant raw material to EH (Morales et al., 2017). Several studies and reviews in the last years include generically softwoods, mixed softwoods or refer mostly to spruce and fir as a source for bioethanol production (Pan et al., 2005; Wingren et al., 2008; Inoue et al., 2016; Alvarez-Vasco and Zhang, 2017). Literature about bioethanol production from pines is limited, and specifically about South-American pines is non-existent. A summary of pretreatments attempted in the last years to increase enzymatic digestibility of pine substrates is shown in Table 3.

Most relevant pretreatments studied to increase enzymatic digestibility of eucalyptus substrates are shown in Table 4.

For a better visualization of the relationship between processes and EH, the pretreatments referenced in Table 3 and 4 were grouped in order of EH as low, medium, and high, and were schematized as shown in Figures 2, 3, and 4 (pine) and Figures 5, 6, and 7 (eucalyptus). Since references were heterogeneous in the form to express EH yields, the non-comparable schemes were excluded.

General studies have stated that dilute acid hydrolysis followed by EH is a promising technology for all raw materials, including pines (Galbe and Zacchi, 2002; Chandel et al., 2007). Nevertheless, the achieved digestibility is rather low in spite of the increasingly complex quantity and the variety of pre-treatments tested for pine in the last two years (Tian et al., 2016; Rajagopalan et al., 2017; and others listed down in Table 3).

Most studied processes for pines include mechanical and acid pretreatments followed by alkaline or organosolv delignification. Results of EH are generally poor, with few cases above 90%. Best digestibilities (EH > 90%) were obtained on sawdust, using alkaline treatments without a previous additional stage. The only exception was a case of radiata pine but it may be ascribed to its comparatively low density, as mentioned in Section 2. The operational conditions of the pretreatment methods are defined according to the physical and chemical characteristics of the raw material and determine the characteristics of the treated substrate. The digestibility of pine with high lignin content is low, so some lignin must be extracted (Meier, 2015; Kruyeniski et al., 2016a). The intention of acid pretreatments is to extract hemicelluloses to increase porosity, but it does not result in an improvement in the EH of pines because of lignin condensation, being harmful to its final form and use (Sannigrahi et al., 2008; Stoffel et al., 2014). In conclusion, new processes must be developed and optimized to improve the digestibility of resinous pines.

Like for pines, the best results for eucalyptus EH (between 90% and 100%) could be obtained by delignification treatments. Nevertheless, in this case, the inclusion of a previous additional stage involving hot water with or without acid (acid hydrolysis or autohydrolysis generated by the deacetylation of xylans) could lead to enhanced EH. Unlike pines, it is possible to apply a combination of acids, alkalis, and solvents when handling eucalyptus without producing a significant condensation of lignin, to obtain high EH yields and byproducts (Figures 3, 4, 6 and 7). This allows the extraction and exploitation of hemicelluloses and lignin in the biorefinery context. However, the recovery of chemicals and the scale of production should also be taken into account when delignifying processes such as kraft or sulfite are included. On the contrary, the application of treatments such as ionic liquids or complex solvents seems not to be so effective in enhancing the EH of these hardwoods. It is also clear that high enzyme charges would not be needed to increase digestibility if the correct pretreatment would be applied.

Comparing the EH data in the different schemes, it is evident that eucalyptus wood is less recalcitrant to EH than pine wood, and that there is already a sufficient study background to define applicable pretreatment technologies with smaller adjustments.

Almost all reports on pines and eucalyptus indicate that pretreatments should involve mechanical treatment for size reduction of the raw material as well. This is unnecessary when using wood wastes like sawdust, which is a basic advantage reducing costs and technological complexity. However, studies on pretreatments for bioethanol production from both

Table 3.
Summary of pretreatments methods used for pine and their corresponding enzymatic digestibility.

Raw material*	Origin	Pretreatments and conditions	Maximum enzymatic digestibility	Reference
Southern yellow pine sawdust	USA	Supercritical CO ₂ treatment: 3100 psi, 165°C, 30 min EH: Cellulase enzyme complex (200mg/g substrate), 50°C, 72 h	Untreated: 12.8% Treated: ≈17.6% (w/w)	Kim and Hon (2001)
<i>Pinus contorta</i>	Canada	1. Steam explosion treatment: 200°C, 4.0% SO ₂ (w/w), 5 min 2. Organosolv delignification: ethanol:water 65:35% (v/v) + 1.1% SO ₄ H ₂ , 170°C, 60 min EH: cellulase (20 FPU) and β-glucosidase (40 IU), 45°C, 48 h + addition of Surfactants	1+2 Without surfactant with EH≈ 60% With surfactant with EH: ≈ 90%	Tu et al. (2007)
<i>Pinus contorta</i>	Canada	Organosolv delignification: ethanol:water 65:35% (v/v) + 1.1% SO ₄ H ₂ , 187°C, 60 min EH: cellulase (20 FPU) and β-glucosidase (40 IU), 50°C, 48 h	100% cellulose to glucose yield	Pan et al. (2008)
Red pine	USA	Sulfite treatment to overcome recalcitrance of lignocellulose (SPORL): 1. Magnesium bisulfite 8% odw(w/w), 3.68% odw sulfuric acid, 30 min at Tmax (180°C) 2. Atmospheric disk milling (disk gap 0.25 mm). EH: Cellulase (20 FPU/g cellulose) and β-glucosidase (30 CBU/g cellulose), 50°C, 72 h	1+2100% cellulose conversion	Zhu et al. (2009)
<i>Pinus rigida</i>	South Korea	Organosolv delignification: 50:50% (v/v) ethanol:water+ a. 1% SO ₄ H ₂ b. 1% MgCl ₂ c. 2% NaOH 170-210°C, 20 min EH: Cellulase enzyme complex 50°C, 72 h	a. 55–60% b. 60% c. 80%	Park et al. (2010)
<i>Pinus taeda</i>	USA	1. Mechanical treatment (milling): pass a 5 mm screen 2. Organosolv delignification: 65% ethanol/water solution, 1.1% SO ₄ H ₂ , 170°C, 1 h EH: cellulase (8 FPU/g cellulose) and β-glucosidase (16 IU/g cellulose), 50°C, 80 h	1 + 2 70%	Sannigrahi et al. (2010)
Pine wood chips	USA	Mechanical treatment: Extrusion (single screw extruder), 3:1 compression ratio, 150 rpm screw speed, 180 °C barrel temperature EH: cellulase (15 FPU/g) and β-glucosidase in a 1:4 ratio , 50°C, 48 h	65.8% of cellulose recovery	Karunanithy et al. (2012)
<i>Pinus taeda</i> chips (1.0× 2.0 × 0.3 cm)	USA	Organosolv delignification: 65% ethanol, 1.1% (w/w) SO ₄ H ₂ , 170°C, 60 min EH: cellulase (20 FPU/g) and β-glucosidase, 2% consistency (w/w glucan), 48°C, 72 h	70%	Li et al. (2013)
Loblolly pine	USA	Alkaline delignification: 1. Kraft process: H factor 1500, 18% active alkali, 25% sulfidity 2. Oxygen delignification: 0.7 MPa, 6% NaOH, 110°C, 60 min 3. Refining: PFI mill, 9000 rev EH: Cellulase enzyme complex (10 FPU/g substrate), 50°C, 96 h	1+2+3 Sugar yield: 87.6%	Wu et al. (2014)
Pine	Iran	Mechanical treatment (milling): 20-80 mesh 1. Hot water treatment: 180°C; 60 min 2. Organosolv delignification: 75% (v/v) ethanol + 1% w/w SO ₄ H ₂ ; 180°C, 15 min + 60 min EH: Cellulase enzyme complex, (25 FPU/g oven dry weight biomass), 45°C, 72h	1. + 2. ≈25%	Amiri and Karimi (2016)
Pine	Iran	Mechanical treatment: Milling, particles less 1mm 1. Ultrasonic irradiation: input power 355 W, frequency: 45 kHz, 60°C; 60 min 2. Anaerobic biological treatment: inoculum 40 mL, substrate 0.5 g, deionized water 10 mL; 27 days, 37°C EH: cellulase (30 FPU/g) and β-glucosidase(50 IU/g), 45°C, 72 h	1 + 2= 27.3% 2= 17.5%	Bahmani et al. (2016)
<i>Pinus taeda</i> L.	USA	Organosolv delignification:55% ethanol, 1% SO ₄ H ₂ ,170°C, 60 min EH: Cellulase enzyme complex (60 FPU/g glucan), 48 h, 55°C	≈ 75% yield	Heringer (2016)
<i>Pinus taeda</i>	USA	Mechanical treatment (milling): 0.5-1.0 mm size particles. 1. Alkaline hydrogen peroxide (AHP): 50 g/ L KOH, 50 g/L H ₂ O ₂ ; 78° C; 24 h. 2. Ethyl-hydro-oxides (EHOs): 60% ethanol (of total solution); 50g/L KOH, 50g/L H ₂ O ₂ ; 78°C; 24h EH: Cellulase enzyme complex (80.2 FPU/g biomass), 50°C,72h	1. AHP: 61.84 ± 1.08% 2. EHOs: 75.18 ± 0.85%	Jain and Bridges (2016)
<i>Pinus strobes</i> L.	Canada	Mechanical treatment (milling): pass 80-mesh sieve. Organic electrolyte solution (OES): room temperature ionic liquids (RTILs) + polar organic solvent: DMSO + 0.1 to 0.9 [AMIM]Cl EH: Cellulase enzyme complex(16.6 FPU/ g biomass), 50°C, 120h	Without treatment: 10.5 ± 0.2% 63.0 ± 2.3% with χ _{[AMIM]Cl} = 0.8	Tian et al. (2016)
<i>Pinus radiata</i>	Chile	Organosolv delignification: 50:50% (v/v) ethanol:water,1.1% w/w H ₂ SO ₄ ,189°C, 8 min EH: Cellulase enzyme complex (0.044 g/g dry pretreated material), 50°C, 72h	Hydrolysis yield: 82.94 ± 1.34%	Valenzuela et al. (2016)

Table 3.
(Continued).

Raw material*	Origin	Pretreatments and conditions	Maximum enzymatic digestibility	Reference
<i>Pinus elliottii</i> sawdust	Argentina	Alkaline extraction + diluted acid treatment: a. Acid hydrolysis b. Steam explosion c. a + O ₂ EH: Cellulase (20 FPU/g glucan) and β-glucosidase (40IU/g glucan), pH 4.8, 50°C, 72h	a. 7.5% glucose b. 24% c. 36%	Stoffel (2016)
<i>Pinus elliottii</i> sawdust	Argentina	Alkaline and alkaline organosolv delignification: a. NaOH-AQ: 55.17 g/L NaOH, 140min, 170°C, LSR: 5/1 b. NaOH-Ethanol: 50 g/L NaOH, 35/65 ethanol/water, 60 min, 170°C, LSR: 5/1 EH: Cellulase (20 FPU/g glucan) and β-glucosidase(40IU/g glucan), 50°C, 72h	a. 96,9% b. 91,1%	Kruyeniski et al. (2016a)
<i>Pinus radiata</i>	New Zealand	Mechanical treatment: 1. Thermomechanical stage: 5 min atmospheric steaming, 80°C + 1 st compression screw (3:1 ratio) + 72 min steaming, 7.5 bar (173°C) + 2 nd compression screw 2. Milling: pressurized disc-refining + 60 min wet ball-milling EH: Cellulase enzyme complex (20 FPU/g substrate), 50°C, 24h	1+2= 80%	Suckling et al. (2017)
<i>Pinus pseudostrabus</i> sawdust	Mexico	Acid + alkaline treatments: 1. Nitric acid: 10.9% HNO ₃ ; 30 min; 114.8°C 2. Sodium hydroxide 1% NaOH EH: Cellulase enzyme complex (25 FPU/ g of total carbohydrate), 48°C, 72 h	1. + 2. 99.2% reducing sugars/ cellulose in the pretreated material	Farfas-Sánchez et al. (2017)
<i>Pinus eldarica</i>	Iran	Mechanical treatment: Milling, particles less 1 mm Dilute alkaline treatment: 2% (w/v) NaOH, 180°C, 5 h EH: Cellulase enzyme complex + hemicellulase, 48°C, 72 h	78 %	Safari et al. (2017)

EH: Enzymatic hydrolysis

* As appears in the original reference.

Table 4.
Summary of eucalyptus pretreatments and their corresponding enzymatic digestibility.

Raw material*	Origin	Pretreatments and conditions	Maximum enzymatic digestibility	Reference
<i>Eucalyptus globulus</i>	Spain	HCl-catalysed acid delignification: 70% acetic acid, 0.025% HCl, 160°C; 1 h EH: 50°C, 48 h	50%	Vazquez et al. (2000)
Six species, mainly <i>Eucalyptus globulus</i>	Japan	Acid catalyzed organosolv delignification: EtOH/water: 75/25, 200°C, 60 min, 1 wt.% acetic acid on liquor + Pulverization: ball milling EH: 50 mg of pretreated wood in 17 mL of acetate buffer, 2 mg enzyme, 45°C, 48 h	100%	Teramoto et al. (2007)
Eucalyptus	Japan	Hot-compressed water (HCW): 160°C, 30 min + Mechanical treatment: ball milling 20 min. EH: 4 FPU/g substrate, 72 h, 45°C	66.7% (on sugar content in dried eucalyptus)	Inoue et al. (2008)
<i>Eucalyptus globulus</i>	Spain	Hot water autohydrolysis: 250°C (4.0 MPa) EH: 10,3 FPU/g substrate and 10 β-glucosidase 10 IU/FPU, 96 h, 48.5°C	100% cellulose-to-glucose conversion (high degradation cellulose in the pretreatment, 79% recovery)	Romaní et al. (2010)
<i>Eucalyptus globulus</i>	Spain	Hot water treatment: 198°C + Organosolv delignification: 60 kg ethanol/100 kg liquor; LSR: 8 g liquor/g oven-dry autohydrolyzed wood; 1 h EH: 10.3 FPU/g pretreated material, and β-glucosidase/cellulase ratio = 5 IU/FPU, 48.5°C, 72 h	100% calculated (agree with experiences) for So: 3.65-3.94 and T: 180-200°C	Romaní et al. (2011)
<i>Eucalyptus globulus</i>	Spain	Water pre-extraction: immersion for 16 h at 25°C + Steam explosion: 1.08 MPa (183°C), Severity factor= 3.56, two cycles: 10 min and 3min + Laccase-mediator system + Mechanical treatment: milling to particles < 1 mm. EH: Cellulolytic complex 20 EGU/g+ b-glucosidase (1:3ratio), 50°C, 72 h	27.1%	Martín-Sampedro et al. (2012)
<i>Eucalyptus grandis</i>	Korea	Alkali catalyzed steam explosion: impregnation: 7 wt.% NaOH + Steam explosion: 210°C, 9 min. EH: 50°C, 72 h, 30 FPU/g glucan	65.5% glucose recovery	Park et al. (2012)

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Table 4.
(Continued).

Raw material*	Origin	Pretreatments and conditions	Maximum enzymatic digestibility	Reference
<i>Eucalyptus globulus</i>	Spain	Hot water autohydrolysis: T _{max} 230°C. EH: 16 FPU/g, 35°C, 96 h	Maximum ethanol conversion in SSF: 91%; 67.4 g/L	Romaní et al. (2012)
<i>Eucalyptus globulus</i>	Chile	Alkaline delignification: Kraft pulping: 155°C, 20% AA, 30 min EH: 20 FPU and 40 IU/g of pretreated material, 50°C, 96 h	Glucans conversion 100%	Monroy et al. (2012)
<i>Eucalyptus dunniithinnings</i>	Australia	Mechanical treatment: milling (particle size 1.0 mm - 1.4 mm) + Soaking in acid: 0.5% H ₂ SO ₄ (v/v), 60 min, room temperature + Microwave treatment: 195°C; 7 min EH: dosed 1.25% (protein n cellulose), 50°C, 48h	74% conversion of theoretical cellulose	McIntosh et al. (2012)
<i>Eucalyptus nitens</i> (EN) <i>E. globulus</i> (GLO) <i>E. urograndis</i> (URO)	USA	Alkaline delignification: Kraft pulping: 150°C, 10:1 liquor:wood, 40% AA, 25% sulfidity, 60 min EH: Cellulase and β-glucosidase, 20 FPU/g on dry weight of the substrate, 50°C, 48h	94.7% (EN) 97.9% (GLO) 80.2% (URO)	Santos et al. (2012)
<i>Eucalyptus</i>	China	Dilute acid treatment 160°C, 0.75% SO ₃ H ₂ , 10 min EH: 20 FPU/g dry matter, 50°C, 60 h	32.19% Glucose	Wei et al. (2012)
<i>Eucalyptus globulus</i>	Spain	Four cycles: <i>M. thermophila</i> laccase (50 U / g) - mediator methyl syringate (3%) + Peroxide-reinforced alkaline extraction: 1% (w:w) NaOH, 3% (w:w) H ₂ O ₂ (odw), 80°C, 90 min EH: Cellulase (2 FPU/g) and β-glucosidase (100 nkat/g), 45°C, 72h	55.7% (glucose/sample weight)	Rico et al. (2014)
<i>Eucalyptus</i>	Japan	Mechanical treatment: milling + pulverizing to particles <0.2 mm + Hot water autohydrolysis: 150°C, 4 h EH: High solid saccharification (32%), 0.04 mL Optimash BG/g of dry substrate, 24 h	76% glucose yield based on the sugar content in the pretreated sample	Fujii et al. (2014)
<i>Eucalyptus grandis</i> sawdust	Brazil	Biological pretreatment: white-rot fungi: <i>Pleurotostreatus</i> EH: Cellulase (from <i>T. Reesei</i> added to obtain a final activity of 10 U/mL), 37°C, 48 h	48.0 μmol reducing sugars/mL	Castoldi et al. (2014)
<i>Eucalyptus urophylla</i>	China	Hot water pretreatment: 240°C; 30 min + Alkaline fractionation: 2% NaOH; 90°C; 2.5 h EH: 17 FPU/g and 34 IU/g dry weight of substrate, 50°C, 72 h	95.6%	Sun et al. (2014)
<i>Eucalyptus grandis</i>	Australia	Diluted acid: a. 4.8 wt.% H ₂ SO ₄ ; 190°C; 15 min b. 2.4wt.% H ₂ SO ₄ ; 180°C; 15 min + Steam explosion (pilot-scale) EH: 20 FPU/ g glucan, 50°C, 72 h	a. 68.0% b. 71.8%	McIntosh et al. (2016)
<i>Eucalyptus globulus</i> L.	Chile	Mechanical treatment: 0.5–1 mm × 0.5–1 mm high × 10–20 mm + Ionic liquid: 1-N-ethyl-3-methylimidazolium acetate (C2minOAc), 1:3 wtwood:wt IL; 150°C a) 30 min b) 60 min EH: 37 FPU/ g cellulose and 4.9 CBU/ g cellulose, 50°C, 72 h	Sugar yield (theoretical value of carbohydrate in biomass, wt-%): a. 65.8 b. 82.2	Lienqueo et al. (2016)
<i>Eucalyptus urophylla</i> x <i>E. grandis</i>	Brazil	Alkaline pretreatment: 10% NaOH (o.d.); liquor:biomass = 2:1; 175°C; 90 min to T _{max} ; 15 min at T _{max} ; H factor = 628 Mechanical treatment: milling to 20/80 mesh size EH: 15 FPU/ g substrate 50°C, 72 h	0.18 g glucose/g biomass	de Carvalho et al. (2016)
<i>Eucalyptus grandis</i> x <i>E. urophylla</i>	China	Mechanical treatment: 80–100 mesh + Solvent extraction: methylbenzene–ethanol, 2:1 v/v, 6h + Ionic liquid: 1-butyl-3-methylimidazolium acetate ([Bmim]OAc) Alkali treatment: 4.0 % NaOH, 90°C, 2 h, 1:20 (g/mL) EH: 15FPU/g substrate, 50°C, 72 h	[Bmim]OAc: 62.6% [Bmim]OAc + alkali treatment: 90.5%	Li et al. (2016)

EH: Enzymatic hydrolysis ; T: Temperature ; So: Severity factor

* As appears in the original reference

sawdust of regionally-growing species are unanimous in stressing on the need for conditions adjustment for any of these raw materials (Stoffel et al., 2014; Rangel et al., 2016).

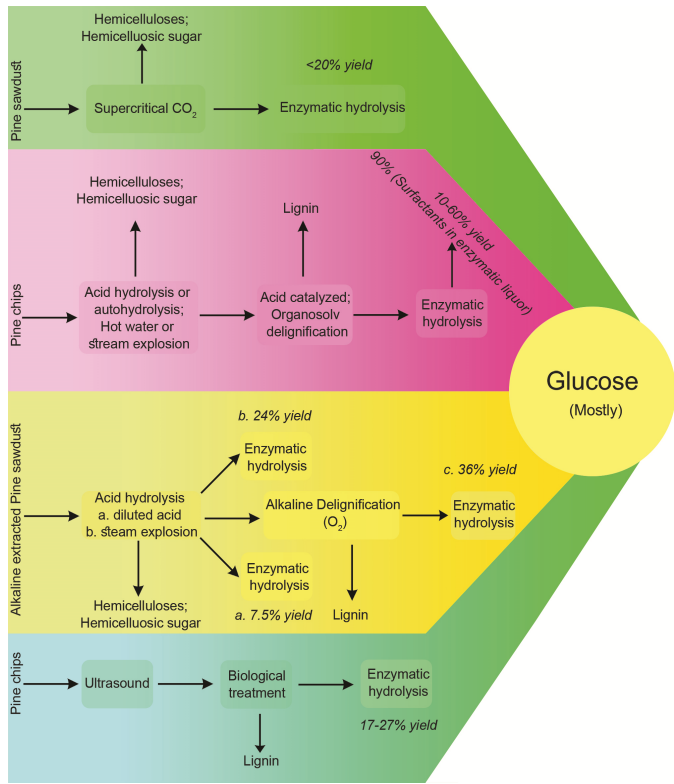


Fig.2. Schematic representation of reported pretreatments on pine producing low enzymatic hydrolysis yields.

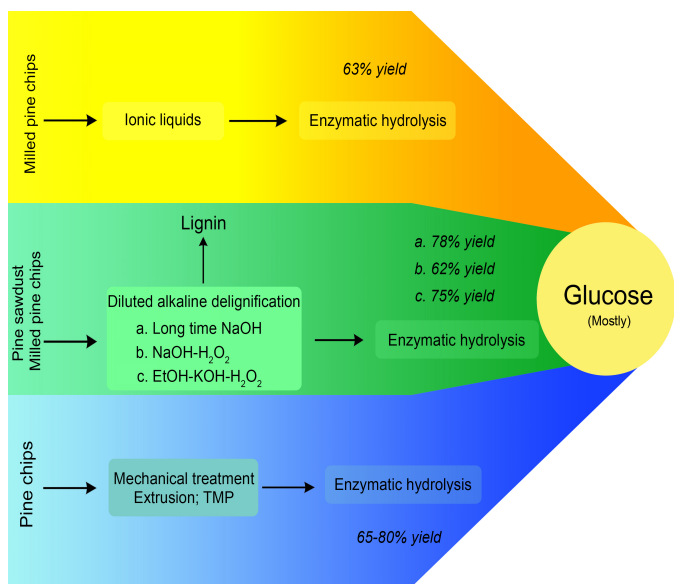


Fig.3. Schematic representation of reported pretreatments on pine producing medium enzymatic hydrolysis yields.

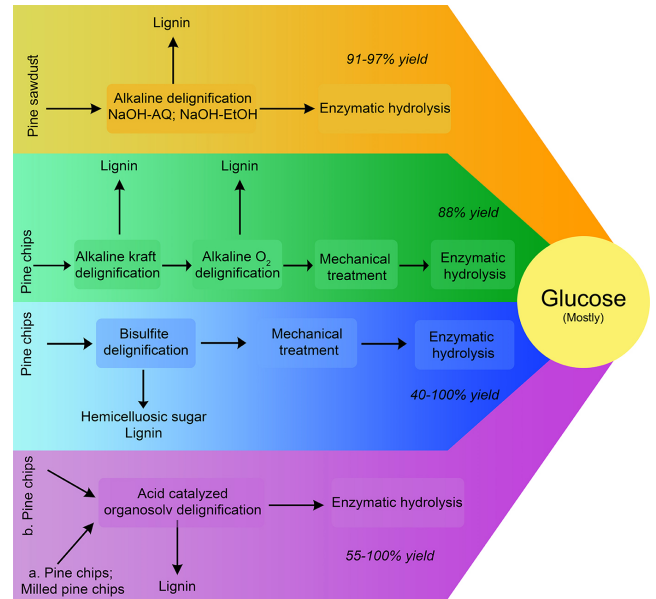


Fig.4. Schematic representation of reported pretreatments on pine producing high enzymatic hydrolysis yields.

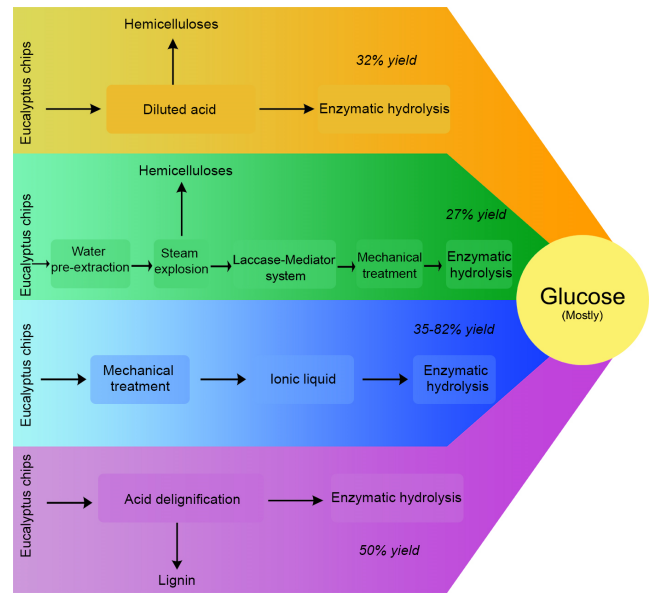


Fig.5. Schematic representation of reported pretreatments on eucalyptus producing low enzymatic hydrolysis yields.

Ethanol yields are usually expressed in comparison with the theoretical yield, i.e., 0.511 g of ethanol/g hexose. Like in the case of the EH, ethanol yields are influenced by the raw material, the pretreatment, and the fermentation process, which can be Separate Hydrolysis and Fermentation (SHF) or Simultaneous Saccharification and Fermentation (SSF). In several cases, it is also necessary to apply a detoxification process to eliminate

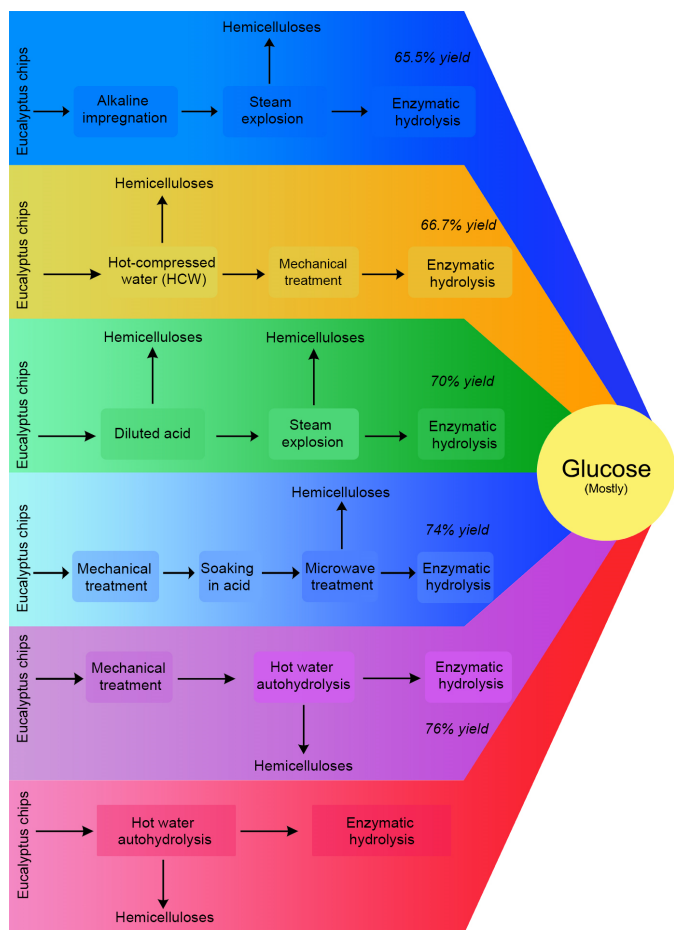


Fig.6. Schematic representation of reported pretreatments on eucalyptus producing medium enzymatic hydrolysis yields.

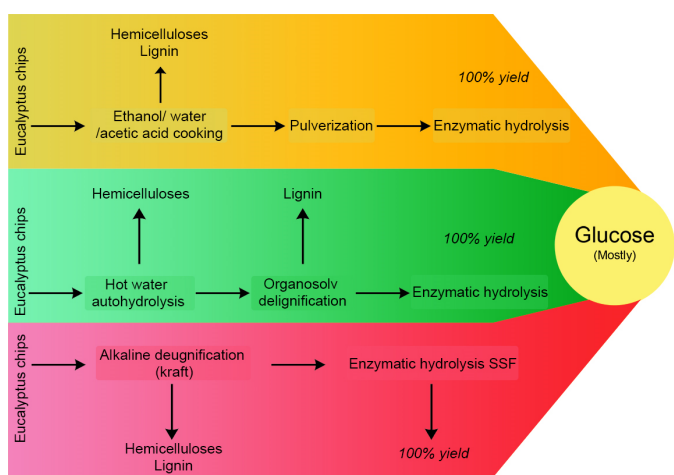


Fig.7. Schematic representation of reported pretreatments on eucalyptus producing high enzymatic hydrolysis yields.

fermentation inhibitors such as 5-hydromethyl-furfural (HMF), furfural, or acetic acid among others (Hahn-Hägerdal et al., 2006). Reported ethanol yields obtained from pretreated pines with methods resulting in low to medium saccharification (Table 3 and Figures 2 and 3) were generally low, in the range of 28% (Bahmani et al., 2016) to 46.6% (Tain et al., 2016), using an SHF process. On the contrary, delignified materials present high ethanol yields, either using SHF or SSF, for example, 80.42% with an SSF process (Valenzuela et al., 2016), 88% with an SHF (Fárias-Sánchez et al., 2017), and about 90% applying an SHF process (Kruyeniski et al., 2016b). Ethanol yields in the case of eucalyptus are usually high, without differences among materials subjected to acid hydrolysis or delignification. Based on the data reported in the selected works tabulated in Table 4, an ethanol yield of 86.4% was obtained by the SSF of a hydro-thermally pretreated material at 230°C (Romaní et al., 2010) and 92% was obtained with an SHF process using a material pretreated by diluted acid (McIntosh et al., 2012). Furthermore, the ethanol yield of the SSF of a kraft pulp was 96% (Monroy et al., 2012) while that of an organosolv-pretreated pulp stood at 91.1% (Romaní et al., 2011). Nevertheless, the ethanol yield of the SSF of wood pretreated by an ionic liquid resulted in only 38% (Lienqueo et al., 2015), while that of the pre-saccharification simultaneous saccharification fermentation (PSSF) of eucalyptus wood pretreated by diluted acid and steam explosion at pilot scale was 42% (McIntosh et al., 2016). This conforms that certain pretreatments lead to physicochemical changes in the materials used which may not be positive for the EH nor for fermentation.

4. Technical and economic aspects of bioethanol production

As mentioned earlier, second-generation bioethanol is still under development at pilot and pre-commercial scales. In better words, its economic feasibility at large scale has not yet been justified because of its high costs, which are two to three times more expensive than petroleum fuels considering an equivalent energy basis (Lynd et al., 2005; Carriquiry et al., 2011; van Eijck et al., 2014; Achinas and Everink, 2016). Nevertheless, the production cost can be decreased by: (i) improvement in feedstock production and logistics, (ii) increase in energy efficiency of the processes involved (i.e., pretreatment, saccharification, and fermentation) and (iii) the production of multiple products (Carriquiry et al., 2011; Melin et al., 2011). On the other hand, in most cases, energy cost determines the global process cost. Therefore, energy savings by optimizing the operating conditions of the different systems are essential to increase profit margin and reduce emissions (Kemp, 2007).

Overall, developing suitable pretreatments to minimize energy consumption and to improve enzymatic saccharification and fermentation are key to achieve high sugars and ethanol yields. Any given pretreatment process can be evaluated through its energy efficiency and the attainable sugars yield (Zhu and Pan, 2010; Walker, 2011; Kang et al., 2014). In biorefineries, the pretreatments implemented could affect the downstream processes, the scale-up, and the technological scheme. The type of pretreatment could also determine the chemical recovery processes and the wastewater treatment. In general, scale-up is a technological challenge that involves high capital investments, as well as detailed research and development (Naik et al., 2010; Aditiya et al., 2016; Muktham et al., 2016).

As mentioned in the previous section, size reduction (increasing surface area) of wood chips by milling could improve the enzyme accessibility to cellulose. Unlike agricultural wastes, wood chips milling requires high electric-mechanical energy, approximately 500 to 800 kWh/ ton, which is equivalent to 25 - 40% of the thermal energy produced by the ethanol. Therefore, pretreatments that need a prior size reduction, e.g., those with ionic liquids (IL), should take into account this energy demand (Zhu et al., 2010). An alternative to size reduction is the use as feedstock of sawmills wastes such as sawdust because these lignocellulosic materials do not require size reduction.

On the other hand, by performing size reduction of wood chips after chemical treatment, an energy savings of about 80% could be achieved. So, the cellulosic pulping industry has a high potential for bioethanol production, and its treatments, processes, and equipment are technologically exchangeable. Other benefits of size reduction after a chemical treatment are a better separation of the pretreated solids from the liquid, energy savings in mixing with respect to the pretreatment of

fiberized or pulverized materials, and a reduction of thermal energy in the chemical treatment due to the use of low liquid-to-solid ratios (LSR). Fiberized materials require high LSR because they have much more water intake than wood chips, and consequently, they need a greater thermal energy for heating up the water or liquor (Zhu et al., 2010; Vallejos et al., 2012, 2015 and 2017).

Temperature and LSR mainly govern the thermal energy consumption in chemical pretreatments, so the reduction of these parameters is critical for the increase of their energy efficiency (Balan, 2014; Kang et al., 2014). The pretreatments with IL are carried out at temperatures below 100°C but require LSR of 10 to 20 (Tian et al., 2016). Although the temperature is low, high LSRs increase the thermal energy consumption to values greater than the thermal energy of aqueous thermochemical pretreatments. For example, the required energy at 75°C and LSR of 10 is 18% more than that required at 180°C and LSR of 3 (Zhu et al., 2010). The performance of different pretreatments at varied LSR was studied in several works (Saska and Ozer, 1995; Garrote et al., 2003; Carvalheiro et al., 2004 and 2008; Chen et al., 2010; Rangel et al., 2016; Testova et al., 2009; Vallejos et al., 2012 and 2015).

The production of multiple products is key to have competitive production cost against the first-generation biofuels and that depends on the pretreatment processes. Several high-value products can be produced through the second-generation biorefineries to reduce the overall processing cost of biofuels (Stephen et al., 2012; Balan, 2014). Lignin is an aromatic polymer usually used in the pulp and paper industry to generate energy (heat and power). Regional pines can be a valuable source of vanillin, which is produced from lignin at large commercial scale and competes with vanillin based on guaiacol derived from petroleum (Pinto et al., 2013). On a smaller scale, bakelite, resins, and plastic filler materials can also be produced and new byproducts will surely be obtained from lignin based on catalytic processes in the following years. The type of recovered lignin depends on the treatments used to remove it from the biomass. For example, high purity isolated organosolv lignin can be used for producing high valued byproducts (Hubbe, 2015). Isolated lignin from a steam explosion or dilute acid pretreatments is highly condensed and can be used for energy generation through producing products like pellets or bricks (Stephen et al., 2012).

Important aspects to take into account when starting a business of this type are the costs of feedstock, enzymes, and capital since they are crucial in defining the costs of second-generation bioethanol. According to a calculation made in the year 2016, the contributions of the costs of each one of these factors to bioethanol production cost was USD 0.26/L for feedstock, USD 0.26–0.40/L for enzymes, and USD 1.85/L for capital investment, including on-site enzyme production (Araújo, 2016).

Bioethanol production costs depend on the biomass source and only a few kinds of biomass having prices close to fossil fuels can be competitive. For bioethanol to compete economically with petrol, production costs should be no greater than EUR 0.2/L approximately. Some bioethanol production costs from wood are EUR 0.44 - 0.63/L for spruce (softwood), EUR 0.48 - 0.71/L for willow (hardwood), and EUR 0.11 - 0.32/L for wood wastes (Walker, 2011). The great advantage of using low-cost sawing waste is accordingly very clear.

Estimations for Brazil in the year 2020 show that eucalyptus production costs, specifically as raw material for bioethanol, will be 2.4-3.3 USD/GJ generated, involving mainly fertilizers and harvesting costs. The technological scheme proposes a pretreatment sequence including mechanical and acid treatments followed by enzymatic saccharification of the residual solids and fermentation of sugars. The investment costs for a capacity of 400 MWth would be USD 374 million (van Eijck et al., 2014).

Moreover, a techno-economic analysis on the production of second-generation bioethanol concluded that high-performance enzymes at a price less than USD 18.2/L of ethanol would be required and that higher ethanol concentration in the fermentor would be needed to be competitive (Kazi et al., 2010). The reduction in the hydrolysis time while maintaining the same yield would also result in a reduction of capital cost. Improvements could also be achieved through the implementation of the SSF. Further research is still needed in this domain to achieved significantly higher level of optimization of the processes involved.

Energy integration, chemicals recovery, higher capacities, and integration of the ethanol plant with already existing facilities, could also reduce the ethanol production cost (Von Sivers and Zacchi, 1995). As examples, the combination of enzymes recycling and decreases in hydrolysis time led to decreased ethanol production cost by 27% for hardwoods and 38% for softwood feedstocks (Gregg et al., 1998). The co-location of the bioethanol plant into a softwood

kraft-pulping mill, using the kraft process plus oxygen delignification as pretreatment were also shown to result in economic production of bioethanol (Wu et al., 2014). More specifically, an economic analysis showed that through such implementations, an ethanol yield of 285 L/ton of dry wood with a total production cost of USD 0.55/L could be obtained (Wu et al., 2014). In this sense, it would be interesting to evaluate how the incorporation of a different pretreatment to a different raw material (like pin-chips or sawdust) would work, taking advantage of the existing infrastructure of the mill.

5. Conclusions

Eucalyptus and pines are the most important woody raw materials in South America. Most processes applied as pretreatments to pine begin with a reduction in the size of the materials by grinding, except in the case of delignifying processes that, in general, work directly with chips. Treatments with diluted acid, steam explosion or supercritical CO₂, aimed at the extraction of hemicelluloses, slightly affect the digestibility of the material. If acid-treated pine wood is delignified, the yields of EH increase but to a less extent than when the delignification treatments are applied to the untreated materials. Materials treated under mild conditions (slightly acidic or alkaline processes, including organosolv delignification), generally have lower EH yields than either medium or highly alkaline treatments. The above are conclusions generally drawn, a few cases have been mentioned in which treatments with diluted acids and diluted alkalis led to high EH yields though. This could be ascribed to the variations in the materials used affecting the subsequent delignification or in better words, to the particular characteristics of the raw materials (pine).

Eucalyptus wood is less recalcitrant to EH than pine wood, so autohydrolysis and alkaline pretreatments are effective options. Novel and more complex treatments or treatment combinations are being studied, but EH yields do not exceed that of alkaline delignification.

Like in the case of the EH, ethanol yields are influenced by the raw materials, the pretreatment, and the fermentation process. The differences between pines and eucalyptus observed in the EH are reflected in the yields of ethanol obtainable from pretreated materials.

Overall, the success of the second-generation bioethanol depends on its technical, environmental, and economic feasibility. The price of the lignocellulosic raw material is one of the most important items in the cost distribution of second-generation bioethanol, whence it is clear the great advantage of using low-cost sawing waste. Biorefineries can also contribute to the reduction of the overall processing cost of bioethanol production by processing wood wastes, using energy and cost-effective technologies, and simultaneous production of high added-value products.

Second-generation bioethanol could generally be regraded as a viable option to valorize the residues of the forest industry in South America. This could be well explained by the highly economically available and unexploited wood residues generated by the fast-growing plantations in Argentina, Brazil, Chile, and Uruguay on one hand and the growing interest in further development of renewable energies in the region on the other hand.

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