



# Wood residue (*Pinus patula* bark) as an alternative feedstock for producing ethanol and furfural in Colombia: experimental, techno-economic and environmental assessments



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## HIGHLIGHTS

- *Pinus patula* bark for producing ethanol and furfural on a biorefinery concept.
- Experimental, techno-economic and environmental assessments were carried-out.
- Alkaline, dilute acid and liquid hot water pre-treatments were tested.
- The system is profitable by consider heat integration and lignin valorization.
- The environmental impacts are decreased after heat integration and lignin valorization.

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## ABSTRACT

This study investigates the technical, economic and environmental performances for producing ethanol and furfural from *Pinus patula* bark, on a biorefinery concept. This was done through experimental, techno-economic and environmental assessments. The experimental analysis considered the physicochemical characterization of the raw material and three pre-treatment methods: (i) dilute acid, (ii) alkali, and (iii) liquid hot water. The alkali method showed the highest yield (50%) and the pentose rich hydrolysate was used to produce furfural (yield 91%). The solid from the pre-treatment stage was enzymatically hydrolyzed (max. concentration 63 g/l), and the hexose rich solution was used as substrate for producing ethanol (0.42 g ethanol/g sugars). The obtained experimental yields were used as the basis to build a process model to generate mass and energy balances, from which the techno-economic and environmental assessments are derived. Based on different levels of heat integration, three scenarios were assessed: (Sc.1) non-integrated, (Sc.2) fully energy integrated and (Sc.3) fully integrated plus cogeneration scheme. Results revealed that by increasing the level of energy integration, the biorefinery system can be profitable with a positive net present value (Sc.3: 184.54 M.USD/y) and a payout period within the project's life-time (Sc.3: 2.22 y). The annualized production costs can be decreased up to 84% and 66% for scenario 3 in comparison with scenarios 1 and 2, respectively. From the environmental point of view, the biorefinery system is positively affected by increasing the level of energy integration. The potential environmental impact can be reduced up to 74% and 66% for scenario 3, in comparison with scenarios 1 and 2, respectively.

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## 1. Introduction

The world's economically recoverable fossil fuels become less plentiful, and uncertainties in oil prices and volatility are currently

a reality. Due to this and future constraints on carbon dioxide emissions, many countries have set up policies to support the production and use of first generation biofuels (e.g., USA, China and Brazil) (Havlík et al., 2011). However, due to sustainability concerns such as land use and the debate on food security, there is a great interest on producing fuels from lignocellulosic biomass due to its abundance, potential lower costs than energy crops, potential land use change reductions and non-competition with food (Fujieda et al., 2012; Havlík et al., 2011; Quintero et al., 2013;

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Wiloso et al., 2012). The development of technologies to produce energy and chemicals from lignocellulosic biomass, as alternative to petroleum-derived products, have prompted biomass valorization to become an important area of research to establish a sustainable bio-based economy.

Bioethanol is a promising renewable alternative for the partial replacement of fossil fuels. Currently, the worldwide production of bioethanol is mainly derived from starch and sugar based feedstocks such as beets, sugarcane and corn. Lignocellulosic ethanol is not commercially available yet, since it is still hampered by economic and technical obstacles (Quintero et al., 2013; Sánchez and Cardona, 2008). Different residues, including corn stover (Grohmann and Bothast, 1997; Öhgren et al., 2007; Wang and Chen, 2011), rice straw and hulls (Karimi et al., 2006; Oberoi et al., 2010; Quintero et al., 2013), cotton stalks (Silverstein et al., 2007), sugarcane bagasse (Adsul et al., 2005; Quintero et al., 2013; Roberto et al., 1991), empty fruit bunches (Quintero et al., 2013), and coffee cut-stems (Quintero et al., 2013) have been investigated as potential sources of cellulose for bioethanol production.

Furfural is an important basic non-petroleum chemical and a versatile key derivative produced from pentose-rich biomass (Mamman et al., 2008). Sugars can also be dehydrated via chemical catalysis to yield furfural (from 5-carbon sugars like xylose), which is considered as a selective solvent for organic compounds and a building block for its transformation into potentially viable components of the P-series fuels or liquid alkanes (Aristizábal et al., 2015). For instance, (Chareonlimkun et al., 2010) produced furfural from the hemicellulosic fraction of biomass through an hydrolysis process, and later use it as a source for the synthesis of transportation fuels such as ethyl levulinate (ELV), dimethylfuran (DMF), and gamma-valerolactone (GVL) (Chhedha et al., 2007).

*Pinus patula* is a soft wood with applications in the wood industry of Colombia, in which important amounts of residues are produced. There are no official data regarding the actual production of *Pinus patula* for the wood industry in Colombia, and only (Gómez et al., 2012) claimed that approximately 12–20% of the total production volume was used in the wood industry. Based on field surveys, (Mejía-Jaramillo and Rendon-Cardona, 2006) estimated that the *Pinus patula* processing generated approx. 65% of residues and only the 35% was used as end wood product. One of these residues are *pinus* barks with no commercial uses in Colombia according to the reported by (Ospina-Penagos et al., 2011). At mid and long term, this can become an important environmental issue. Additionally, there is a great opportunity for the economic exploitation of these type of residues. Thus, the residues derived from the processing of *Pinus patula* become an interesting raw material for the production of biofuels and chemicals adopting the biorefinery concept (El-Halwagi, 2012; Moncada et al., 2013; Posada et al., 2012).

Based on the described above, the aim of this work is to assess the technical, economic and environmental feasibility of producing bioethanol and furfural from *Pinus patula* bark. For this, experiments and techno-economic and environmental assessments were carried out. The physico-chemical composition of *Pinus patula* bark is experimentally determined and different pre-treatment alternatives are experimentally tested (i.e., dilute acid, alkali and liquid hot water). Additional experiments on the enzymatic saccharification of cellulose, fermentation of the cellulose rich hydrolysate into ethanol, and dehydration of the pentose rich hydrolysate into furfural are also carried out. The yields of the pre-treatment, saccharification and fermentation stages as well as the raw material characterization were used as data inputs for a process model that was built to generate the mass and energy balances, which are the inputs of the techno-economic and environmental assessments. Based on different levels of energy

integration, three scenarios are assessed from the techno-economic and environmental points of view.

## 2. Materials and methods

### 2.1. Raw materials

The *Pinus patula* barks were collected and dried at room temperature (22–28 °C) and milled to a particle size of 400 µm in a bench-top Vibratory disc mill (Retsch SR 200). These were obtained from a local producer in the west central region of Colombia (Manizales-Caldas).

### 2.2. Characterization methods

#### 2.2.1. Physicochemical analyses

*Pinus patula* barks were characterized to determine its cellulose, hemicellulose, lignin, ash, extractives, and moisture contents. The moisture content was determined by drying the material to constant weight (the difference of weight constitutes the moisture content). The extractives were determined by using a water-ethanol mixture based on the procedure reported by the National Renewable Energy Laboratories (NREL) (Sluiter et al., 2005). The total lignin content was determined as the sum of Klason lignin and acid-soluble lignin according to the standards of the Technical Association of Pulp and Paper Industry (TAPPI) T-222 om-83 and TAPPI 250UM-85, respectively (Han and Rowell, 1997; Sluiter et al., 2008). The cellulose content was calculated after holocellulose content, which was quantified by further treatment of the obtained fibers with sodium hydroxide and acetic acid (Rowel and Young, 1997; Sluiter et al., 2010). The hemicellulose content was calculated by subtracting the cellulose content from the holocellulose content (Rowel and Young, 1997; Sluiter et al., 2010). The ash content was determined after the total ignition of the samples at 575 °C for 4 h according to TAPPI standard T211 om-93 (Han and Rowell, 1997).

### 2.3. Experimental procedure

#### 2.3.1. Pretreatment of raw material

Studies on different pre-treatment methods were performed, in which the production of sugars (mainly C5 sugars) was evaluated. The pre-treatment methods were: (i) diluted acid, (ii) alkali, and (iii) liquid hot water. For diluted acid and alkali pre-treatments, the procedure was carried out in an autoclave at 121 °C for 1 hour. The pre-treatment with liquid hot water was performed at 135 °C for 2.5 h. The percentage of H<sub>2</sub>SO<sub>4</sub> and NaOH was 1% (v/v) and the solid to liquid (S/L) ratio was 1/10. After the thermal treatment, samples were cooled to room temperature and the hydrolysate containing the released sugars (mainly C5 sugars and inhibitors) was separated by filtration. The filtrated liquid fraction was used for the production of furfural. The pre-treated biomass slurry was used as raw material for the saccharification process. Experiments were performed by duplicate and the average value was reported.

#### 2.3.2. Enzymatic hydrolysis (saccharification)

Enzymatic hydrolysis was carried out with a commercial Cellulase, Celluclast<sup>®</sup> 1.5 L and multienzyme complex Viscozyme L. The biomass slurry (rich in cellulose) obtained during the pre-treatment stage, was washed with hot water to remove possible inhibitors that might still been attached to the solid matrix (which may affect the yield and rate of the enzymatic hydrolysis step). The amount of substrate was 15 g and the enzyme dosage was 25 filter paper units (FPU) per g of cellulose or substrate. The reaction volume was 100 ml and the pH was adjusted using a 0.1 M citrate buffer solution (pH 4.8–5.0). Next, the saccharification process was

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