Stand-alone and biorefinery pathways to produce hydrogen through gasification and dark fermentation using *Pinus Patula*

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**A B S T R A C T**

New efforts in the search of alternative clean and renewable energy to replace the current energy predecessors have been assessed in order to reduce emissions to the environment. Lignocellulosic Biomass (LB) can be used to produce bioenergy due to its high energy potential and availability. Different ways are proposed for the transformation of these residues into high added-value products. Thermochemical and biochemical technologies are the most interest concepts focusing on the use of biomass as source for energy production at positive net balances. This study presents the techno-economic, energy and environmental assessment of five scenarios for the hydrogen production through gasification and dark fermentation based on the biorefinery and stand-alone concepts. The results demonstrated that the production of hydrogen based on the concept of a biorefinery can improve the profitability, energy efficiency and reduce the emissions of the processes compared to that based on the stand-alone way. The selection of ethanol and electricity as valuable co-products of the biorefinery in the hydrogen production process confirmed that the process scale and products diversity makes possible a flexible and suitable process to produce hydrogen and other energy carriers from *Pinus Patula*.

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1. Introduction

High energy consumption, reduction of fossil fuel storages, emissions related to greenhouse gases, among others, have increased interest in the search of new renewable energy sources. Colombia is a country suitable for agriculture, nevertheless, the main energy source is the oil which contributes up to 40% of the primary energy generation (FAO, 2014). In last years, Colombia has been promoting the use of lignocellulosic biomass, especially from agribusiness processes, to obtain high added-value products (i.e. cogeneration processes to obtain electricity from sugarcane bagasse (Asocaña, 2014)). However, the lack of energy policies in Colombia has hindered the implementation of new technologies for the proper use of these residues.

*Pinus Patula* (PP) is widely distributed in Colombia and has become a useful timber specie for reforestation programs. Its main use is for the production of sawn wood. According to the Agricultural and Rural Planning Unit (UPRA), Colombia has a total area of 214.000.000 Ha from which only 12% is suitable for forestry plantations, corresponding to approximately 24.000.000 Ha. However, due to technical and legal restrictions, only the 55% of the suitable area for forestry plantations can be used for the implementation of reforestation programs, representing today about 200.000 Ha. Different forestry species are cultivated in Colombia, such as the *Eucalyptus globulus*, *Tectona grandis* among others. Nevertheless, *Pinus Patula* is the most used specie in forestry plantations due to the high cultivation yield that ranges from 12 to 22 m³ Ha⁻¹ year⁻¹, justifying more than 70.000 Ha used in Colombia for this purpose. Then, the residues produced during PP processing (practically not used today) are an interesting alternative for obtaining added value products. Other advantages of the PP to be used in the reforestation programs are related to its multiple applications and also the non-intensive silviculture practices. Recollection and transportation logistics of wood residues are the main drawbacks for their use as energy source for bioenergy production. As a consequence, woody materials have been used in combustion process for cooking and heating water where the energy efficiency is very low.

The high dependence of the main economic sectors in Colombia on the fossil fuels highlights the necessity of implementing new technologies to produce high-impact products with high energy...
potential considering the large amount of wastes generated at different stages of the agroindustrial and forestry supply chains. There are different methods to transform these residues into bio-energy products. Thermochemical processes (i.e., gasification, combustion and pyrolysis) have been gaining importance due to they can use an extensive range of biomass and have a high productivity. In contrast, biochemical processes such as dark fermentation to produce hydrogen (as well as fermentation processes to obtain second generation ethanol) require more research for its implementation. However, it can be an alternative for bioenergy production with low energy consumption (Ghimire et al., 2015).

Hydrogen is nowadays a promising source of energy that can be used directly and indirectly as storage fuel with less environmental issues, especially without CO₂ emissions (Parthasarathy and Narayanan, 2014). However, only 4% of hydrogen is produced from renewable sources since high percentage of residual biomass is used directly as feedstock for combustion processes where its energy density is lower (Udomsirachakorn and Salam, 2014; Panagiotopoulos et al., 2009). Several authors have studied the efficiency of operating parameters such as temperature, moisture content, air/biomass ratio in biomass gasification and the effect of temperature, pH, substrate concentration and fermentation time in dark fermentation for hydrogen production (Dejtrakulpong and Patula, 2014; Hameed et al., 2014; Lv et al., 2007; Nisslå et al., 2014; Ntaikou et al., 2010; Urbaniec and Bakker, 2015).

The aim of this work is to develop a techno-economic, energy and environmental assessment of five scenarios for the hydrogen production through gasification and dark fermentation using *Pinus Patula* as energy source. Two scenarios were taken as base cases which involve the stand-alone thermo-chemical and biochemical production of hydrogen, and the three remaining scenarios were evaluated based on the biorefinery concept for different configurations. The techno-economic evaluation was performed considering the effect of the hierarchy distribution of the products in the hydrogen production cost. The energy and environmental assessment was carried out in order to compare the energy efficiency and CO₂ emissions of the stand-alone and biorefinery pathways, respectively.

2. Methodology

In order to evaluate the performance of a stand-alone and biorefinery ways to produce hydrogen, five scenarios were proposed. Two scenarios are related to the production of hydrogen in a stand-alone pathway from which only one product was obtained. The remaining three scenarios were evaluated considering the conceptual design of a biorefinery which is related to three concepts: i) hierarchy, ii) sequence and iii) integration (Moncada et al., 2014). First corresponds to the hierarchical decomposition of relevant elements in the biorefinery, such as feedstocks, products, and technologies. Then, the logical order of the technologies and products in the biorefinery must be decided (sequence). And finally, it is analyzed the convenience of the integration of the raw materials, processes or process streams if needed (Sánchez and Cardona, 2012).

According to the hierarchy approach, the first step considers the selection of the main products that are going to be the targets for the design and can be categorized in five groups: biofuels, bio-energy, biomolecules and natural chemicals, biomaterials, and food product. Hydrogen, electricity and ethanol were selected as main products addressing the hierarchy in design to hydrogen, then to ethanol and finally electricity. Then, the sequence of the technological routes was established according to the well-known onion diagram, giving importance to the reaction stage (Moncada et al., 2013). Finally, the integration of the stream processes that can be used as energy sources in other processes was carried out. Mass and energy balances were obtained using simulation procedures. The software used for this purpose was the simulation tool Aspen Plus v8.0 (Aspen Technology, Inc, USA).

The effect of the hierarchy of products within a biorefinery was used to evaluate the economic performance of hydrogen production. The main objective of this procedure was to select which scenarios, in a biorefinery way, make the process more profitable compared to those in a stand-alone pathway. Additionally, it was calculated the energy efficiency of each scenario to support the selection of the most suitable process. There must be a balance between economic profitability and environmental impacts of the process to be considered as sustainable. As a consequence, Green House Gases (GHG) assessment was performed in order to calculate the amount of CO₂ emitted by each scenario.

2.1. Process description

2.1.1. Gasification

Gasification consists in the transformation of carbonaceous materials (i.e., lignocellulosic biomass) into synthesis gas with high content of hydrogen, carbon monoxide, carbon dioxide and methane using as gasifying agent. The hydrogen production process through biomass gasification can be divided in three stages: Raw material pretreatment, biomass gasification and hydrogen separation and purification. Particle size and moisture content are the key parameters in the pretreatment stage due to the possibility of changing the hydrogen content and the gasification performance according to the value of these parameters. Zainal (2001) evaluated the effect of the biomass moisture content in the hydrogen composition and calorific value of the generated gas in a downdraft gasifier. High moisture content increases hydrogen production but the calorific value of the syngas decreases due to the high energy requirements to evaporate the water and thus, promoting exothermic reactions which produce CO₂ and H₂O. Small particles have larger surface area and therefore faster heating rate which affects the product gas composition (Lv et al., 2004). For simulation purposes, a particle size of 0.5–1 cm and a moisture content of 20% were selected based on the best values proposed by these authors.

The second stage is related to the chemical pathway of gasification that takes place inside of the reactor as shown in equations (1)–(8). The simulation of the downdraft gasifier is performed splitting the reactor in three main processes: pyrolysis, combustion and reduction. Dried biomass undergoes into the devolatilization (pyrolysis) where the raw material is decomposed into carbon, hydrogen, oxygen and ash according to the elemental analysis. Then, all the components from pyrolysis zone goes into the combustion chamber where they react with oxygen to produce CO₂, CO, H₂O and heat. The char produced in the pyrolysis and the combustion zone passes to the reduction zone where char gasification takes place to produce CO₂, CO, H₂ and CH₄. Ash and the remaining char are separated from the syngas using a cyclone.

In order to improve the hydrogen content in the generated gas, a catalyst adsorption is proposed. Carbonation reaction is based on the conversion of carbon dioxide (CO₂) into calcium carbonate (CaCO₃) using calcium oxide (CaO) as catalyst. Udomsirachakorn et al. (2014) evaluated the production of hydrogen from steam biomass gasification using as catalyst CaO and it was demonstrated that the concentration of CO₂ decreases, enhancing the water-gas shift reaction in order to produce more H₂ and CO. For this reason, a coupled two bed reactors using CaO as catalyst were chosen to improve the selectivity of the hydrogen in the synthesis gas.

Finally, a further purification stage is required using hollow fiber
membranes which are widely used in many gas separation industries (Feng et al., 2013). Previous treatment of the hydrogen rich gas is required to reach the suitable pressure conditions inside the membrane in order to enhance the mass transfer of the hydrogen. According to Maus et al. (2008) the filling pressure that must be supplied from the hydrogen storage location should be at levels of 35–70 MPa. For this reason, due to the loss of energy after the membrane separation, the hydrogen stream must be compressed to reach the required conditions for the filling station. Subsequently, the high pressure hydrogen stream can be used to generate steam which can meet the heating requirements of the process. The process scheme used in the production of hydrogen through biomass gasification is presented in the Fig. 1.

\[ \text{Pyrolysis} \]
\[ \text{Biomass} + \text{heat} \rightarrow \text{C}_5 + \text{tar gases} \]  

\[ \text{Combustion} \]
\[ \text{C}_5, \text{tar gases} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{heat} \]  

\[ \text{tar gases} + \text{heat} \rightarrow \text{CO} + \text{H}_2 \]  

\[ \text{Reduction} \]
\[ \text{C}_5 + \text{CO}_2 \leftrightarrow 2\text{CO} \]  

\[ \text{C}_5 + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2 \]  

\[ \text{C}_5 + 2\text{H}_2 \leftrightarrow \text{CH}_4 \]  

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \]  

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]  

2.1.2. Electricity generation

The generated synthesis gas from the biomass gasification has a high energy content which can be used directly as fuel in a gas engine to produce electricity due to the high H$_2$/CO ratio. An internal combustion engine burns the gaseous fuel to produce electricity by means of a generator. Normally, the efficiency of these devices are between 27 and 38% and they can provide energy in form of electricity from 30 kW h to 60 MWh (UPME, 2003).

2.1.3. Ethanol fermentation

Wood residues have high cellulose and hemicellulose content, from which fermentable sugars for the bioenergy production can be obtained. Due to high cellulose crystallinity and low biodegradability, lignocellulosic biomass may require a pretreatment prior to fermentation processes (Nissila et al., 2014). For this reason, a mild-acid pretreatment and enzymatic hydrolysis are proposed as methods for raw material pretreatment. Acid hydrolysis under mild conditions is the main process used for saccharification of lignocellulosic biomass. Rafiqul and Mimi Sakinah (2012) evaluated the performance of the dilute acid hydrolysis of Meranti wood at different sulfuric acid concentrations (2–6%wt.) and residence time (0–120 min). Highest acid concentration (6%wt.) enhanced the content of xylose and glucose and reduced the residence time to 20 min. On the other hand, low xylose and glucose concentration and higher residence time (>100 min) are obtained when the process was carried out with a low acid concentration (2%wt.). In this study, sulfuric acid (6%w/w) at 130 °C was used to obtain mainly xylose as carbon source for the ethanolic fermentation. One problem associated with the dilute-acid hydrolysis is the formation of toxic compounds such as acids, furfural and phenolic compounds. As a consequence, detoxification reaction is proposed as an alternative to transform these compounds into other less toxic substances that may not inhibit the cell growth. Alkaline treatment with Ca(OH)$_2$ is widely used in the hydrolysates detoxification (Taherzadeh et al., 2000). The unconverted fraction of cellulose from the acid hydrolysis can be used to produce glucose by enzymatic saccharification. Two types of enzymes (Cellulase and b-glucosidase) at 50 °C were used in this process (Cardona et al., 2004).

The fermentable sugars obtained from the pretreatment stage are converted into ethanol using the bacteria *Zymomonas mobilis* at 30 °C for 30 h. This bacteria has the ability to degrade hexoses and pentoses, as carbon source (Leksawasdi et al., 2001). Then, the fermentation broth with an ethanol concentration of 5–6% by
2.2. Scenarios

The production of hydrogen as a single product from gasification and dark fermentation was evaluated scenarios considering three products (hydrogen, ethanol and electricity) for the gasification of Pinus Patula. The process scheme for the ethanol production from Pinus Patula is presented in Fig. 2.

2.2.1. Dark fermentation

Dark fermentation is a complex process that involves diverse groups of bacteria where simple sugars or disaccharides are converted into hydrogen, carbon dioxide and organic acids (Urbaniec and Bakker, 2015). As mentioned in section 2.1.3, different pretreatment methods are implemented in order to obtain fermentable sugars to be used in fermentation processes, in this case for biohydrogen production.

The hydrolysate obtained from the acid and enzymatic treatments can be used as carbon source for hydrogen production by the moderate thermophile Thermoanaerobacterium thermosaccharolyticum. Hydrogen, carbon dioxide and other metabolites (ethanol, acetic acid, butyric acid, among others) are the main products from the dark fermentation. The separation of hydrogen from the carbon dioxide can be performed using coupled porous and non-porous membranes in order to enhance the selectivity of the hydrogen. Authors (Belaafi-bako et al., 2006) evaluated the performance of a porous and non-porous membrane for the separation of hydrogen from a fermentative process. In the biotechnological process, a recovery percentage up to the 70% can be reached. Furthermore, the separation of ethanol as main byproduct is also performed using the same downstream process described in section 2.1.3. The process scheme used for the production of hydrogen through dark fermentation is illustrated in Fig. 3.

2.2. Scenarios

Five scenarios for gasification and dark fermentation were proposed in order to evaluate the effect of the hierarchy decomposition of the products in the economic, energy and environmental assessment of the hydrogen production. Stand-alone ways (the production of hydrogen as a single product from gasification and dark fermentation) were selected as base cases for the comparison with the remaining three scenarios in which the conceptual design of a biorefinery was applied. Table 1 shows the description of the five evaluated scenarios considering three products (hydrogen, ethanol and electricity) for the gasification scenarios and two products (hydrogen and ethanol) for the dark fermentation scenarios.

Scenarios 1 and 4 consider only the production of hydrogen from the stand-alone processes. Two additional scenarios are proposed for the production of hydrogen, ethanol and electricity through biomass gasification. Scenario 2 considers the use of 50% of the generated syngas in the gasification for hydrogen production and the remaining 50% for the electricity generation using the syngas as fuel in a gas engine. Furthermore, scenario 3 considers the ethanol production from a fraction (30%) of the Pinus Patula fed in the process. The remaining 70% is used in the gasification process for syngas production from which, 50% is used in hydrogen production and the remaining 50% for electricity generation. Finally, the last scenario considers the separation of the principal byproduct from the fermentation broth (ethanol) along with the hydrogen production.

2.3. Simulation procedure

For all proposed scenarios, mass and energy balances were obtained using simulation procedures. The software used for this purpose was the simulation tool Aspen Plus v8.0 (Aspen Technology, Inc, USA). The objective of this procedure was to calculate the requirements for raw materials, utilities and energy needs. Mathematical modelling of the concentration profiles using kinetic models was performed in software packages such as Matlab (MathWorks, USA). Hydrogen production through air gasification was developed using equilibrium models reported by Dejtrakulwong and Patumsawad (2014). Carbonation and calcination reactions were simulated using the kinetic law reported by Nikulshina et al. (2007). Fermentation using Z. mobilis for ethanol production was assessed using the kinetic model reported by Leksawasdi et al. (2001). Dark fermentation for hydrogen production was modeled using a Monod kinetic model reported by Ren et al. (2010). The membranes split fractions were based on the data reported by Kerry (2006).

For the simulation of the biomass gasification, the Grayson-Streed thermodynamic model was used to calculate the activity coefficients of the liquid phase due to the model was developed for systems with high H2 concentration. The Redlich-Kwong equation of state was applied to describe the vapor phase. In the simulation of the dark fermentation, the Non Random Two Liquids (NRTL) was used to analyze the behavior of the liquid phase and the Hayden O’Connell equation of state was selected to describe the vapor phase (López et al., 2009). Additional data such as physical properties were obtained from the work of Wooley and Putsche (1996).

2.4. Energy analysis

The net energy balance (En) of the process is related to the amount of energy in the products (hydrogen (E氢), ethanol (E乙))
and electricity \((E_w)\) depending of the scenario) compared to the energy needs of the process (i.e. heating requirements \((E_{heating})\), power supply \((E_{power})\), among others) and can be expressed as:

\[
E_n = E_{H_2} + E_{\text{EthOH}} + E_w - E_{\text{heating}} - E_{\text{power}}
\]  

(9)

The global efficiency of the process can be defined as the ratio between the net energy balance and the amount of energy available in the raw material. The energy potential of the biomass is defined as the maximum amount of energy that can be obtained from the raw material if it was submitted to a thermal process. The global efficiency of the process can be calculated as follows:

\[
\eta = \frac{E_n}{m_{\text{biomass}} \cdot \text{LHV}_{\text{biomass}}}
\]  

(10)

Where \(m_{\text{biomass}}\) is the mass flux of biomass \((\text{kg/h})\) and \(\text{LHV}_{\text{biomass}}\) is the heat of combustion of the raw material \((\text{MJ/kg})\).

2.4.1. Energy of the products

The energy content of the products can be calculated from the amount of hydrogen and ethanol that is produced in the simulation procedure and the heating value of each product. The heating value is the energy released as heat when a compound undergoes complete combustion. The energy content of the products can be calculated with the following expression:

\[
E_{\text{product}} = m_{\text{product}} \cdot \text{LHV}_{\text{product}}
\]  

(11)

Where \(m_{\text{product}}\) is the mass flux of the product in \(\text{kg/h}\) and \(\text{LHV}_{\text{product}}\) is the heating value of the product in \(\text{MJ/kg}\). The amount of energy produced from the synthesis gas, which is used as fuel in a gas engine, can be calculated considering the engine efficiency in order to determine the amount of useful energy. The equation that describes the power generated from the synthesis gas is shown below:

\[
E_w = \frac{m_{\text{syngas}} \cdot \text{LHV}_{\text{syngas}} \cdot \eta_{\text{engine}}}{C_0}
\]  

(12)

2.4.2. Energy from external sources

The heating requirements \((E_{\text{heating}})\) were taken from the pinch evaluation of the process using the educational software Hint, which uses the pinch methodology to calculate the exchanger network of a process (Martín and Mato, 2008). The software Hint can provided the energy requirements of the process in terms of the needed heating and cooling utilities to supply the energy demand of a specific process. In the other hand, the amount of power \((E_{\text{power}})\) required in the process was calculated from the energy balance in the simulation procedure.

2.5. Economic assessment

A basic equipment mapping adapted to the economic conditions (tax rate, interest of return, operator and supervisor wages, among others) in Colombia was developed to determine the operating costs of the proposed scenarios including the raw materials, utilities, labor and maintenance, general plant and administrative costs. Additionally, the depreciation of the equipment was evaluated considering a project life of 10 years. The mass and energy balances from the simulation procedure were used as a starting point for the economic assessment using the software Aspen Process Economic...
Analyzer v8.2 (Aspen Technology, Inc, USA). The main data used in the economic assessment of the five scenarios is presented in the Table 2.

### 2.6. Environmental evaluation

Green House Gases (GHG) balance is the net amount of greenhouse gases in terms of CO2 emitted into the atmosphere by a process or product, considering all emissions and sinks along a supply chain. The activities and processes involved in the GHG emission calculation are limited based on the system boundaries. In this study, only the gate-to-gate process boundary (i.e. the transformation of raw materials into products) is considered.

### 3. Results

#### 3.1. Process simulation

The production capacities and yields of each scenario were evaluated based on the mass and energy balances from the simulation procedure, as can be observed in Tables 3 and 4. In the gasification scenarios, the hydrogen production rate decreases from the scenario 1 to 3 which can be explained due to scenario 2 uses a fraction of synthesis gas to produce electricity; meanwhile a fraction of the *Pinus Patula* is intended to be used for the ethanol production in scenario 3, whereas scenario 1 uses all the raw material for the production of synthesis gas and hydrogen. Despite of this behavior, the biomass gasification in the three evaluated scenarios seems to have the higher hydrogen production rate in comparison to dark fermentation. Additionally, scenarios 2 and 3 generate electricity using a fraction of the produced syngas in the gasification which could increase the economic profitability of the process due to the economic compensation of a reached low hydrogen yield. Besides, a fraction of the *Pinus Patula* is used to produce ethanol through fermentation in the scenario 3. The downstream process for ethanol purification has a high energy consumption therefore, the amount of power generated by means of the syngas in scenario 3 is lower than in the scenario 2, as it can be observed in Table 4.

The ethanol productivity in scenario 3 is higher than that obtained in the scenario 5. The main reason is related to the fact that the produced ethanol in the dark fermentation is separated from the fermentation broth as byproduct, which could increase the added-value of the hydrogen. Meanwhile, the metabolic pathway of the microorganism is directly developed to produce ethanol as main metabolite and not as a by-product of the process in the scenario 3.

#### 3.2. Energy analysis

The process design under the biorefinery concept can improve the energy efficiency of the process due to the variety of bioenergy products (i.e. electricity and ethanol) that can be obtained from the evaluated scenarios, as can be observed in Fig. 4. However, the energy requirements of each scenario can be considered as the key parameter to define the possible products that can be obtained under a biorefinery concept. This is the case of the scenarios 2 and 3, where two and three products are obtained, respectively. Nevertheless, the energy efficiency of the scenario 2 is greater than that of scenario 3 due to the high energy requirements involved in the separation and purification of ethanol which decreases the energy efficiency of the global process. Biochemical processes have low productivity due to batch regime operation and high energy needs. Therefore, the process efficiency of the scenarios 4 and 5 is lower compared to gasification scenarios. Despite of the high energy requirements in the biochemical processes, the separation of ethanol as main byproduct can improve the efficiency of these systems. Ruggeri et al. (2010) proposed the possibility to recover the fatty volatile acids from the fermentation broth and giving them an energy valorization in order to enhance not only the energy efficiency, but also the economic performance of the dark fermentation.

#### 3.3. Economic assessment

The main objective of a process under the biorefinery concept is to achieve a better use of the raw materials to produce high added-value products. Therefore, the effect of the hierarchical decomposition of the main products in the final hydrogen production cost has been evaluated, as shown in Table 5. The hydrogen production costs decreased by increasing the variety of bioenergy products that can be obtained under the stand-alone (scenario 1) and the biorefinery scheme (scenarios 2 and 3) in the gasification case. The main parameter that affects the behavior of the economic performance of these scenarios is the “allocation factor”, which distributes the total production cost of the process between the main products. In this study, the economic allocation factor was selected for the economic assessment of the five scenarios due to the fact that hydrogen is the product with the highest economic value.

As a result, the process with the lowest hydrogen production cost is the scenario 2 where electricity is also produced. Even the scenario 3, where hydrogen, ethanol and electricity are produced, has a higher production cost due to the high energy requirements and low hydrogen productivity.

As can be evidenced in Table 6, the highest contributions to the total production cost in the gasification scenarios are the raw materials, utilities and fixed (capital depreciation) costs. The main costs involved in the dark fermentation scenarios are the raw materials and utilities costs. The costs of raw materials involve the production and transportation costs of the feedstock from the crop location to the processing plant. Additionally, in these costs are included the additional supplies costs of the process such as the calcium oxide in the biomass gasification or the sulfuric acid in the dark fermentation. The utilities costs are defined by the cooling and heating requirements of the process, which are related to the costs of steam, electricity, cooling water, refrigerants, among others. Finally, depreciation costs correspond to the fixed costs (equipment costs) of each process.

The costs of raw materials in the dark fermentation are higher than that in the gasification scenarios, except in scenario 3 where ethanol is produced. Fermentation of lignocellulosic materials

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Table 2

<table>
<thead>
<tr>
<th>Utilities, raw materials and products prices.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Price</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pinus Patula</em></td>
<td>0.009</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>0.094</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>0.35</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Calcium Hydroxide</td>
<td>0.05</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>0.062</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Fuel Ethanol</td>
<td>0.06</td>
<td>USD/L</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.47</td>
<td>USD/Kg</td>
</tr>
<tr>
<td>Water</td>
<td>1.352</td>
<td>USD/1m</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.1</td>
<td>USD/kWh</td>
</tr>
<tr>
<td>High P. Steam (105 bar)</td>
<td>9.86</td>
<td>USD/ton</td>
</tr>
<tr>
<td>Mid P. Steam (30 bar)</td>
<td>8.18</td>
<td>USD/ton</td>
</tr>
<tr>
<td>Low P. Steam (3 bar)</td>
<td>1.37</td>
<td>USD/ton</td>
</tr>
</tbody>
</table>

a Price based on the statistics of plantain forest residue obtained from (UPME, 2003).

b Based on hydrogen price projections (McKinsey and Company, 2010).
requires intensive pretreatment steps that involve a high consumption of reagents in order to obtain the greatest amount of fermentable sugars and thus, increasing the raw materials costs. The use of membranes and compressors for the separation and purification of hydrogen enhances the utilities costs in the scenarios 1, 2 and 4. Additionally, the scenarios 3 and 5 have higher heating and cooling requirements that involve the downstream processing of the ethanol.

3.4. Environmental evaluation

The concept of biorefinery also includes the utilization of all the process streams in order to reduce the environmental impact that these can generate if they were emitted directly into the environment. According to this, the GHG calculation of the five scenarios was proposed as one of the selection criteria of the suitable scenario for hydrogen production. Fig. 5 presents the GHG net balance for the evaluated scenarios. The negative values in the scenarios 2–5 mean that the amount of CO₂ generated by the outputs is lower than that CO₂ emissions of the inlet streams (raw materials and supplies) and thus, reducing the environmental impact of these scenarios. The scenario 1 has the highest emissions due to the use of the synthesis gas fraction to generate hydrogen from which an exhausted syngas with high content of carbon dioxide and monoxide is released into the environment. The variety of products that is obtained in the scenarios 2 and 3 demonstrated the hypothesis that the hierarchy distribution of the products under the biorefinery concept can reduce the emissions of these types of processes. However, other impact categories that considers the effect of the organic acids in the ground and water sources should be analyzed aiming to determine the real impact of the biochemical technologies.

4. Conclusions

The stand-alone and biorefinery pathways for the hydrogen production were evaluated in order to determine the most important parameters that influence the economic, energetic and environmental performance of the process. Parameters such as the amount of bioenergy products and the processing scale are the most important variables that must be considered to improve the profitability of these processes. Biochemical processes require more research not only in terms of productivity but also in the proper use of metabolites in the fermentation broth. One of the proposed scenarios for hydrogen production through dark fermentation considers the separation of ethanol from the fermentative broth decreasing the hydrogen production cost and also enhancing the global energy efficiency. Further works have to be focused on the separation of the remaining metabolites such as acetate and butyric acid from the fermentation broth as an added-value to the process. Thermochromic methods such as a gasification have the highest

Table 3
Productivities and yields obtained from the simulation procedure.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Production a</th>
<th>Yields a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Units</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>17.69 Ton H₂/day</td>
<td>0.052 Ton H₂/ton wood</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>8.26 Ton H₂/day</td>
<td>0.024 Ton H₂/ton wood</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>6.22 Ton H₂/day</td>
<td>0.018 Ton H₂/ton wood</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>68,198.00 Liters Ethanol/day</td>
<td>201.2 Liters Ethanol/ton wood</td>
</tr>
<tr>
<td>Scenario 5</td>
<td>1.64 Ton H₂/day</td>
<td>0.004 Ton H₂/ton wood</td>
</tr>
<tr>
<td></td>
<td>15,358.00 Liters Ethanol/day</td>
<td>41.5 Liters Ethanol/ton wood</td>
</tr>
</tbody>
</table>

Table 4
Electricity generation.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Power (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 2</td>
<td>27.3</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Table 5
Economic assessment of the gasification and dark fermentation of Pinus Patula.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Production cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen (USD/tonne)</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>3,590.3</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>2,226.2</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>2,755.2</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>35,568.6</td>
</tr>
<tr>
<td>Scenario 5</td>
<td>27,294.9</td>
</tr>
</tbody>
</table>

*NP – No produced in the given scenario, thus production cost was not calculated.
economic yield and energy efficiencies, nevertheless the implementation of these schemes in a biorefinery approach can even increase the profitability of the process due to the wide range of products that can be obtained from the same raw material.

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References


