Thermochemical and Biochemical routes to produce energy from residues: The case of *Pinus patula* as raw material for direct bioenergy and ethanol production

Estefanny Carmona Garcia[1], Jhonny Alejandro Poveda Giraldo[1], Carlos Ariel Cardona Alzate[1].

[1]Universidad Nacional de Colombia sede Manizales, Instituto de Biotecnología y Agroindustria. Laboratorio de Equilibrios Químicos y Cinética Enzimática. Departamento de Ingeniería Química. Manizales, Colombia
[A1] Corresponding author. Tel.: +57 6 8879300x50417; fax: +57 6 8879300x50452.
e-mail: ccardonaal@unal.edu.co

ABSTRACT

Pinus patula (PP) is one of the types of softwood with great production in Colombia due of its fast growth and high crop yield in forest plantations. The use of lignocellulosic biomass to produce high and low value added products is a very interesting idea that has taken force in the recent years. In this sense, the aim of this work is to produce ethanol from *Pinus patula* with experimental yield 0.35 g ethanol/g glucose (69% of the theoretical). But it was necessary concentrate the hydrolysate due to low solids concentration in the enzymatic hydrolysis (15 g/l) and thus, to obtain a higher sugar concentration. For the other hand a simulation of fermentative process of *Pinus patula* was carried out for different process scales, obtaining that for capacities > 6000 ton/day the standalone process can provide positive profits. Additionally, the energy analysis was focused in the comparison of the biochemical (fermentation) and thermochemical (gasification) pathways for energy production, obtaining a greater efficiency for the last one.

Keywords: *Pinus patula, economic and energy analysis, fermentation, ethanol, gasification*

1. INTRODUCTION

Nowadays, the world faces to a reality of serious challenges caused by mismanagement of resources and environmental damage. Some reasons for the economic, social and environmental problems are due to rapid population growth, food and water shortages, greenhouse gas emissions and fossil fuel consumption [1]. The latter is the root and principle of study of many states and government policies, given that oil is the main economic engine in the world [2]–[4]. In an effort to mitigate the consequences of this activity, the implementation of new technologies is urgent as they help to ensure long-term economic growth and sustainability. Fossil fuel substitution enabled the energy and industrial sectors to promote programs and research of environmentally friendly energy [5]. In this way, it was discovered that there was a way to produce renewable and sustainable energy from biomass such as biofuels. The use of these is so extensive that today they represent 40% of the world's total energy consumption [6]. Moreover, it is the innovative approach for developing countries that are characterized by their agricultural abundance, as in the case of Colombia.

Colombia has entered the biofuel sector in the last decade, defining the regulatory framework for the production and commercialization of ethanol and biodiesel in 2001 and 2004 respectively, and began blending them with fossil fuels in 2005 and 2008 [7]. During the year of the ethanol fuel program, the government promoted oxygen enrichment of gasoline to reduce CO emissions from cars, encouraging the gradual conversion of fosil based fuels from cars to E10 (10% ethanol). However, bioethanol produced in Colombia comes exclusively from the processing of sugarcane [8]. In this way, it allows the country's energy sector to promote the implementation of new biomass feedstock with a high cellulosic content for the production of bioethanol, such as coffee wastes, corn, tubers and wood residues such as eucalyptus and pine species.

Pinus patula is a lignocellulosic rich source which is widely distributed in Colombia and is classified as softwood. It is characterized by its high cultivation yields in forest plantations, where it was estimated in 2012 at 12-22 $m^3Ha^{-1}year^{-1}$ [9]. Currently, *Pinus patula* belongs to the national action plan for commercial reforestation, which increases the potential for the development of forestry projects, since Colombia has a reforestation area of $62x10^3$ hectares for this timber species [10], [11]. In this sense, Pinus *patula* allows a high participation in agricultural production and in the employment generation based on the sustainable use and management of natural forests. Its main application is the obtaining of sawmill wood and pulp for the production of kraft papers and packaging. On the other hand, over forest surrounding areas where the

electricity network does not intervene, this wood is used as fuel. Therefore, the generation of waste during the wood processing of *Pinus patula* is a commercial interest for obtaining value-added products that can complement or improve its current use in order to reflect economic and energy efficiencies.

The development of production technologies based on lignocellulosic raw materials have led to an important valorization of biomass in a way that their research interest has been increasing as an alternative to petroleum products [12]. The use of organic waste for biofuel production plays an important role in reducing CO_2 emissions, leading to a high commercial interest in the production of its different products such as biogas, syngas, biobutanol, biodiesel, bioethanol, among others [13]. Bioethanol is the most widely used biofuel worldwide [14], [15]. When the net CO_2 emissions of the life cycle from bioethanol plants are analyzed, this gas can be minimized or eliminated from all emissions involved in raw material cultivation and waste disposal [13]. In this way, bioethanol reduces the impacts of climate change by contributing to the control of air pollution, guaranteeing energy security, promoting local development and providing independence from fluctuations in the market situation and supply of oil.

Bioethanol can be produced from various types of raw materials such as lignocellulosic and algal biomass, sucrose, starch, among others, through ethanol fermentation [16]. The high polysaccharide content in Pinus patula can be hydrolyzed by different physicochemical pre-treatments such as acids or bases, depending on the raw material type, followed by enzymatic hydrolysis (saccharification) [17]–[19] to obtain fermentable sugars. These sugars are then converted into ethanol by fermentation using microorganisms like *Saccharomyces cerevisiae* or *Zymomonas mobilis* [20], [21]. However, during fermentation there are inhibitory characteristics such as temperature, pH, ethanol concentration, fermentation of C5 sugars, fermentation time, stirring speed and inoculum size [6]. Finally, separation technologies are used to recover ethanol before it can be used as a biofuel.

On the other hand, there are other methods of biomass valorization for the production of bioenergy, such as combustion, pyrolysis and gasification. The latter allows the transformation at high temperatures and in the presence of a gasifying agent as oxygen and some solid fuel like biomass, into a gas (syngas) with high energy content. Fuel gas is mainly composed of CO, H_2, CH_4, CO_2 and N_2, where hydrogen is the main product with the highest added value [22]. The syngas usually contains 70-80% of the energy of the original fuel if it is burned [23]. Thus, gasification is an important alternative to combustion because of its ability to use a wide range of raw materials, its high energy content, its economic value and its compliance with pollutant emission standards.

The aim of this work is to evaluate the potential of *Pinus patula* for the production of ethanol trough an experimental and simulation component. For the experimental part the pine was pretreated by dilute acid and enzymatic saccharification, the sugars obtained were fermented by *Saccharomyces cerevisiae* to obtain ethanol. On the other hand, the experimental part had two parts: first the production of ethanol was simulated, including the separation or purification stage and then an economic analysis was carried out using different process scales. Second, a comparison was made between the biochemical route (fermentation) and the thermochemistry (gasification), in order to determine the energy efficiency of each process.

2. METHODOLOGY

2.1 Experimental procedure

2.1.1   *Raw material and reagents*

Pinus patula was used as raw material, collected in a farm located in the central western region of Colombia and dried at room temperature (18-23 °C). To realize the pretreatment were employed sulfuric acid 96% (MERCK) and distillated water. In the enzymatic hydrolysis were used cellulases (Celluclast® 1.5 L), multienzyme complex (Viscozyme® L), citric acid (Disproalquimicos) and sodium citrate (CARLO ERBA) for the buffer solution, and sodium azide solution 2%. For the fermentation were required Freeze-dried *Saccharomyces cerevisiae* strain, D(+)-glucose (MERCK), ammonium sulfate (Panreac), potassium dihydrogen phosphate (MERCK), magnesium sulfate (MERCK), calcium chloride (Panreac) and distillated.

In the sugars determination were used 3,5-Dinitrosalicylic acid (MERCK), sodium hydroxide (MERCK), potassiumm sodium tartrate (Panreac) and distilled water. The chemical characterization of *Pinus patula* was taken from García et al., [24].

2.1.2   Dilute acid pretreatment of Pinus patula

The wood was milled with an upper vibratory disk mill (Retsch SR 200) and sieved to a particle diameter of 0.4 mm. Then the raw material was mixed with a dilute solution of sulfuric acid (2%v/v) in a solid to liquid (S/L) ratio of 1:10, the procedure was carried out in an autoclave at 121°C and 15 psi during 90 minutes [17], [25]. When room temperature was reached, the sample was filtered in a vacuum filtration unit. The liquid phase was stored, in order to determine the concentration of xylose.

2.1.3   Enzymatic saccharification

The solid fraction from the dilute acid hydrolysis was used as raw material for the enzymatic hydrolysis, which was carried out following the protocol NREL/TP-510-42629 [26] with a commercial cellulose (Celluclast® 1.5 L) and multienzyme complex (Viscozyme® L). The process was carried out using a concentration of 15 g/L, an enzyme dosage of 64 filter paper units (FPU) per g of cellulose and 60 p-nitrophenyl-β-glucoside units (pNPGU) per g of cellulose with Celluclast 1.5L and Viscozyme L, respectively. The operation conditions were 72 hours at 50℃, 100 rpm and pH 5 adjusted using a 0.1 M citrate buffer solution. Sodium azide solution 2% was added to prevent the growth of organisms during the saccharification. Afterward, the hydrolysate obtained (rich in C-6 sugars) was separated by vacuum filtration.

2.1.4   Fermentation

The liquid fraction from the enzymatic hydrolysis was used as raw material and freeze-dried *Saccharomyces cerevisiae* was activated for the production of ethanol. Fermentation was performed in 200 mL Erlenmeyer flasks (100 mL working volume) with concentrate hydrolysate, since the sugars concentration obtained in saccharification step is low due to the high solid dilution. The medium was supplemented with minerals: 1.5 g/L $(NH_4)_2SO_4$, 1 g/L KH_2PO_4, 0.3 g/L $MgSO_4$ and 0.05 g/L $CaCl_2$. Experiments were carried out at 32°C and 150 rpm in an incubator (BINDER Incubator BD056) with shaking.

2.1.5   Biomass concentration

The biomass concentration was determined by dry weight method. Therefore, in an Eppendorf tube was placed 1 ml of sample and centrifuged at 10000 rpm for 10 minutes, for this a centrifuge Z 300 K (Hermle Labortechnik GmbH) was used. The supernatant was removed and stored for further analysis. The precipitate was weighed and dried in an oven at 110 ° C for 24 hours and the weight recorded until it is constant.

2.1.6   Sugar concentration

The amount of reducing sugar in the sample was determined using the dinitrosalicylic acid (DNS) method following the procedure proposed by Miller [27]. For the measurement, the supernatants obtained in the biomass determination test are used. In a test tube 500 µl were taken from each sample and 500 µl of DNS reagent were added. The tube was stirred and put into a bath at 90 °C for 5 minutes, then was allowed in cold water for 10 minutes. Afterward, 5 ml of distilled water were added and the absorbance was recorded at 540 nm and by means of a previous calibration curve the concentration of sugars is determined.

2.1.7   Ethanol concentration

The concentration ethanol in the medium was analyzed by Gas Chromatography (GC) using a GC-2014 (Shimadzu) gas chromatograph equipped with a flame ionization detector (FID) and a capillary column Stabilwax. For the measurement, the supernatants obtained in the biomass determination test are used. For each sample, the corresponding dilution was performed and filtered with Millipore filters. The operating conditions of the gas chromatograph were: Injection volume 10 µL, injector temperature: 220 °C, detector temperature: 270 °C, nitrogen as carrier gas with a flow of 0.5 ml/min and running time of 21.75 min.

2.2 Simulation procedure

2.2.1   Fermentation process

The simulation of bioethanol production consists in four stages: pretreatment, enzymatic hydrolysis, fermentation and separation. In this case, a phase equilibrium analysis and the estimation of activity model parameters that describe the thermodynamic phenomenon of the stages involved were taken into account [28]. Initially, the particle size of the dried raw material was reduced trough a milling step, approximately to 2 mm. The milling process was simulated with two gyratory mills. After the milling process, the raw material was hydrolyzed with dilute acid. Dilute-acid pretreatment removes most of the hemicellulose content in the raw material and the conditions chosen were: 121℃, 2 bar, residence time of 15 minutes and solid liquid-ratio 1-10. Then the stream rich in cellulose was carried to enzymatic hydrolysis. A commercial cellulase enzyme is employed in this stage. The conditions to carry out the enzymatic hydrolysis stage were: 50℃, 1 bar, biomass concentration of 15 g/l and enzyme concentration between 2% and 4% [26]. For *Pinus patula* the cellulose conversion to glucose is about 92.65% [29]. The enzymatic hydrolysis stage is the final process in overall pre-treatment process.

Saccharomyces cerevisiae microorganism was used for design the fermentation stage. The production of ethanol begins using the glucose as substrate for fermentation. This stream is fed to a reactor with the biomass in order to produce the ethanol via ethanol fermentation at 30°C. The maximum yield reached by [29] was 0.42 g ethanol per g of sugars (83 % of the theoretical).

After this stage, it was necessary purify the ethanol until 99.5% v/v. For reach this objective, the design of two distillation towers (i.e beer column and rectifying column) was necessary. The beer column is either a stripper with a bottoms reboiler or a direct steam injection column that takes the product from the fermenters and strips out the ethanol overhead. The mash and residual water are removed in the bottoms. The stripped ethanol from the beer column is concentrated in a distillation tower. The overhead product approaches the ethanol/water azeotropic concentration. Final dehydration beyond the azeotropic concentration was done using molecular sieves [30], [31]. The process scheme for the ethanol production from *Pinus patula* is presented in **Fig. 1**.
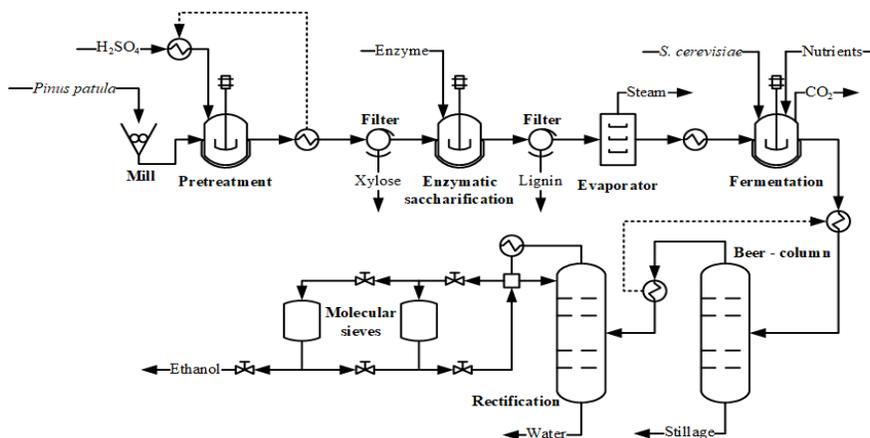

Fig. 1 Scheme of bioethanol production from *Pinus patula*

2.2.2   Economic analysis

The energy requirements (utilities as cooling water, low, mid and high-pressure steam, and electricity) were determined with the package Aspen Energy Analyzer. The cost of the equipment was calculated using the software Aspen Process Economic Analyzer v8.4 (Aspen Technologies, Inc., USA). The capital depreciations, maintenance costs, labor costs, fixed charges, general and administrative costs and the plant overhead were calculated based on the percentages described for the economic assessment of chemical processes of Peters and Timmerhaus [32]. This analysis was estimated in US dollars for a 10-year period at an annual interest rate of 17% (typical for the Colombian economy), considering the straight-line depreciation method and an income tax of 25%. Table 1 presents raw material, utilities and product cost.

Table 1. Prices used in the economic evaluation

RAW MATERIALS	COST	Ref
Pinus patula	40 USD/ton	[20]
Cooling water	0.33 USD/ m^3	[20]
Sulfuric acid	94 USD/ton	[9]
Enzyme	700 USD/ton	[20]
UTILITIES	COST	Ref
Electricity	0.1 USD/kWh	[9]
Low pressure steam (LPS)	7.56 USD/ton	
Medium pressure steam (MPS)	8.18 USD/ton	[9]
PRODUCT	COST	Ref
Ethanol	0.9 USD/kg	[33]

Moreover, the production cost of ethanol was determined and the influence of the process scale (plant processing capacity) in the production costs was assessed according to the six-tenths-factor rule [34], in which the capital cost for equipment increases as a function of throughput according. All results was used as criteria to establish the processing capacity that provides profit margins.

2.2.3   Gasification

The simulation of the gasification was previously described elsewhere [35]. First, the raw material is treated aiming to reduce the particle size and the moisture content. Subsequently, the dried raw material is submitted to a downdraft gasifier. When the gasifying agent is air, the main products are H_2, CO_2, CO, CH_4, N_2, char and ash. In Table 2 is presented the typical gasification products from commercial wood.

Table 2. Typical composition of gas during gasification biomass [36].

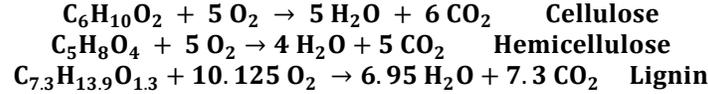| COMPONENT	%
H_2	12-20
CO_2	9-15
CH_4	2-3
CO	17-22
N2	50-54

In Aspen Plus a gasification process can be simulated with four stages: dried, pyrolysis, combustion or oxidation and reduction or gasification. The conditions of each stage were:

Dried: In this stage the raw material is dried, which enters with a humidity of approximately 50% and dries up to 5% [37]. ***Pyrolysis:*** carried out at 700 °C. In this stage there is thermal breakdown the feedstock into C, H_2, and O_2. ***Combustion***: carried out at 1000 °C. At this temperature there are burning of charcoal and tar gases to provide heat for the rest of the processes and the thermal cracking of a portion of the tar gases into

CO, H_2, CH_4 and combustion products. For this stage it is necessary calculate the air inflow to gasifier. For this, the equivalence ratio (ER) is necessary which is calculated with the following equation (Eq.1).

$$ER = \frac{inflow\ air\ gasification}{inflow\ air\ simple\ combustion} \tag{1}$$

In combustion, biomass exothermically reacts with excess air, leading to high reaction rates and high released heat. For lignocellulosic biomass the reactions involved in this process are presented below.

$$C_6H_{10}O_2 + 5\ O_2 \rightarrow 5\ H_2O + 6\ CO_2 \quad \textbf{Cellulose}$$
$$C_5H_8O_4 + 5\ O_2 \rightarrow 4\ H_2O + 5\ CO_2 \quad \textbf{Hemicellulose}$$
$$C_{7.3}H_{13.9}O_{1.3} + 10.125\ O_2 \rightarrow 6.95\ H_2O + 7.3\ CO_2 \quad \textbf{Lignin}$$

With these reactions the oxygen flow required for simple combustion was calculated by stoichiometry. On the other hand, at the equivalence ratio of 0.26, the chemical and total energy of the gas reach the maximum at the carbon boundary. The carbon boundary point (CBP) is the optimum point for operating a gasifier and it is obtained when exactly enough gasifying medium is added to avoid carbon formation and achieve complete gasification [38]. With these values the air flow of the gasification was calculated through Eq. (1).

Gasification: carried out at 1000 °C. Reaction of combustion products and charcoal to produce gaseous fuel (H_2, CH_4) is presented. Syngas is used in other conversion processes, such us in low pressure steam production and electricity cogeneration. This process called **Biomass Integrated Gasification Combined Cycle Technology** [39]. The process scheme for the gasification of *Pinus patula* simulation is presented in **Fig. 2**.
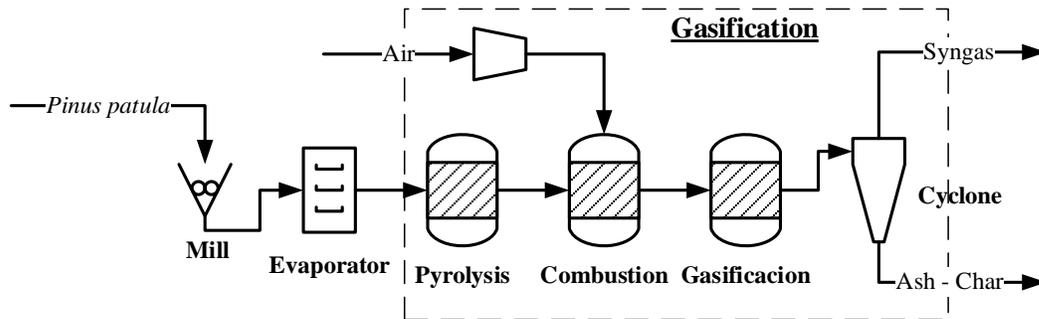

Fig. 2 Biomass integrated gasification with cogeneration system scheme

2.2.4   Energy analysis

Pinus patula can be converted directly or indirectly into energy through different pathways. The most studied ways are biochemical (fermentation) and thermochemical (gasification) ones. In order to compare both technological routes in terms of their energy yield and efficiency. The energetic potential was evaluated considering the gross energy content of the raw material (*Pinus patula*) and the products of each process trough Eq. (2):

$$E = \frac{F_p \times LHV_p}{F_b \times HHV_b} \tag{2}$$

Where E is the energy potential, F_p and F_b are the mass flow of the product and biomass, respectively. HHV_p and LHV_b are the Higher Heating Value of the biomass and Low Heating Value of product, respectively. For calculate the overall process efficiency the utilities requirements must be included in the denominator.

Through the proximate analysis of the raw material (volatile matter, fixed carbon and ash) reported by Garcia [24] and the correlation (Eq. 3) reported by Nhuchhen et al. [40] the calorific value (HHV) of *Pinus patula* was calculated.

$$HHV \left(\frac{MJ}{kg}\right) = 19.288 - 0.2135 \frac{VM}{FC} + 0.0234 \frac{FC}{ASH} - 1.9584 \frac{ASH}{VM} \tag{3}$$

On the other hand, the LHV of the products was calculated as follows: for the product of the biochemical route (ethanol) a reported value was used and for the product of the thermochemical route (syngas) it was calculated by the compositions obtained from the gases and the LHV of the pure compounds.

3. RESULTS

3.1 Experimental procedure

3.1.1 Pretreatment stage

Following the procedure a concentration of reducing sugars of 31 g / L was obtained, which are higher than the results reported by Moncada et al., [20] (20 g/L). This stage is important since it allows making the cellulose matrix more accessible to the enzyme, fragmented hemicellulose to xylose. The solid fraction obtained was used in the enzymatic hydrolysis, obtained a concentration of reducing sugar of 3.02 g/L. After pretreatment and saccharification it was necessary to concentrate the hydrolysate through heating until a concentration of 13.5 g/L, due to the high amount of water used in the enzymatic hydrolysis.

3.1.2 Fermentation

The objective of the experimental part was to evaluate the production of ethanol using *Pinus patula* hydrolysate as a raw material with the microorganism *Saccharomyces cerevisiae*. The initial sugar concentration was 13.5 g/L. **Fig. 3** shows the consumption of total reducing sugars and biomass growth during 69 hours of fermentation. As a result, a substrate consumption of 6.29 g/L was obtained. The final concentration of sugars was 50% of the initial concentration, which suggests that it should be inoculated with a higher concentration of biomass. For the other hand the concentration of biomass in the concentrated hydrolysate was 3.7g/L. It is observed that the lag phase of the microorganism corresponds to the first 5 hours, after this the microorganism started its exponential phase, which suggests that it is not necessary to adapt to the hydrolysate.
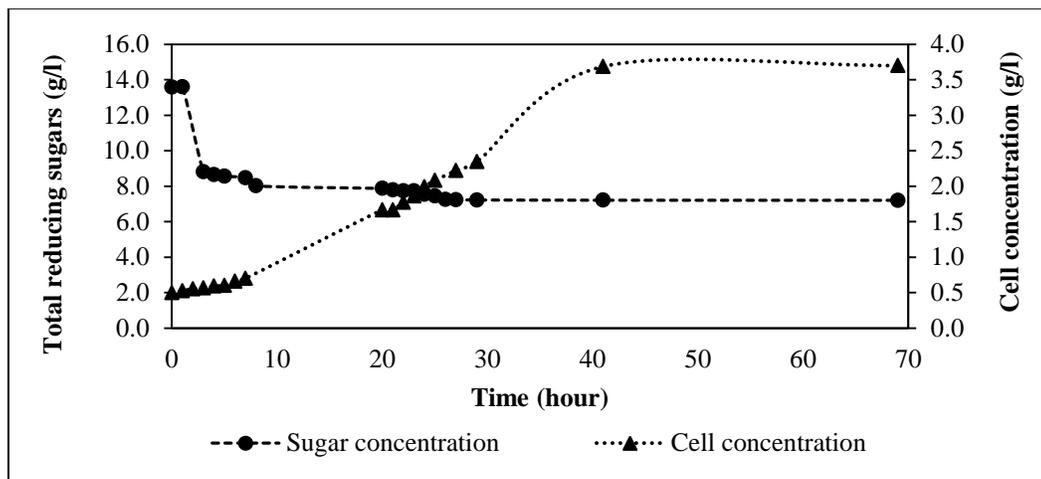

Fig. 3 Biomass growth and total reducing sugars concentration in the ethanol fermentation

The final ethanol concentration was 4.79 g/L, which corresponds to a yield of .035 g ethanol / g sugar (69% of the theorical) which is similar to the yields reported in [41], [42]. Nguyen et al., [43] used softwood chips through direct impregnation with sulfuric acid and steam explosion as pretreatment to produce ethanol using *Saccharomyces cerevisiae.* As a result, ethanol yields between 74 to 89% of theoretical were obtained. Qian et al., [44] studied the fermentation of dilute-acid softwood hydrolysate to produce ethanol using co-cultures of adapted *Sacharomyses cerevisiae* and *Escherichia coli.* The highest ethanol yield from the experimental procedure was 0.45 g/g total sugar. It is observed that the value obtained in this work is similar to the aforementioned reports. On the other, if a higher ethanol concentration is required, the hydrolysate must be concentrated through evaporation until reaching a higher concentration of sugars.

3.2 Simulation procedure

3.2.1 *Fermentation process and economic analysis*

Initially, the simulation was performed for a processing scale of 6000 tons / day. **Fig. 4** presents the contribution of costs of each of the categories evaluated in the economic assessment. It is observed that the category that contributes in greater proportion to the total costs is the raw material. Although its price is low (0.04 USD / kg), its daily volume is high (250 ton / h). From the raw material cost, 55% corresponds to cost of *Pinus patula* (87 mUSD/year), 21% represents the enzymes added for the enzymatic hydrolysis (33 mUSD/year), 19% corresponds to the sulfuric acid used in dilute acid hydrolysis (29 mUSD/year) and 4% for process water (7 mUSD/year). On the other hand, utilities are the second category that most contributes to the cost with 36 mUSD/year distributed as follows: low pressure steam 5.7 mUSD/year, medium pressure steam 13 mUSD/year, cooling water 9 mUSD/year and electricity 7.6 mUSD/year.
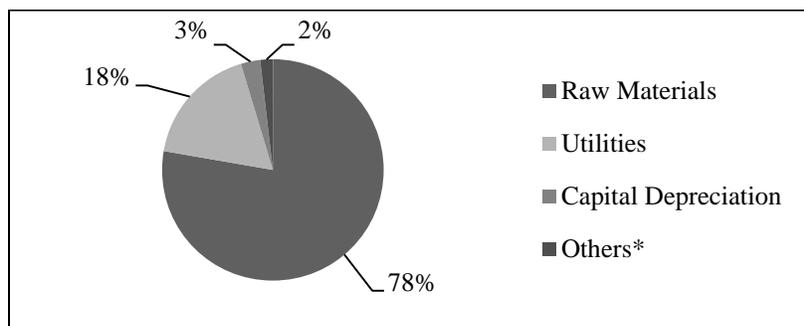
Fig. 4 Cost contribution for the base case (6000 ton/day). *Others corresponds to: maintenance (1.67%), labor (0.12%), fixed and general (1.04%) and plant overhead (0.94)

On the other hand, the production of ethanol is influenced by the amount of raw material that the processing facility is able to transform in bioethanol. For this purpose, a sensibility analysis of different process scales was developed in order to determine which plant capacity should be selected and to decide if the process is economical profitable. Net Present Value (NPV) was used to assess the effect of the process scale in the economics of the process. NPV is the difference between the present value of cash inflows and the present value of cash outflows (including initial cost) over a period of time. In this sense, a process is profitable when its income is greater than its expenses (NPV positive). **Fig. 5** presents the effect of the plant capacity in profitability of the ethanolic fermentation in a period of 10 as project lifetime.
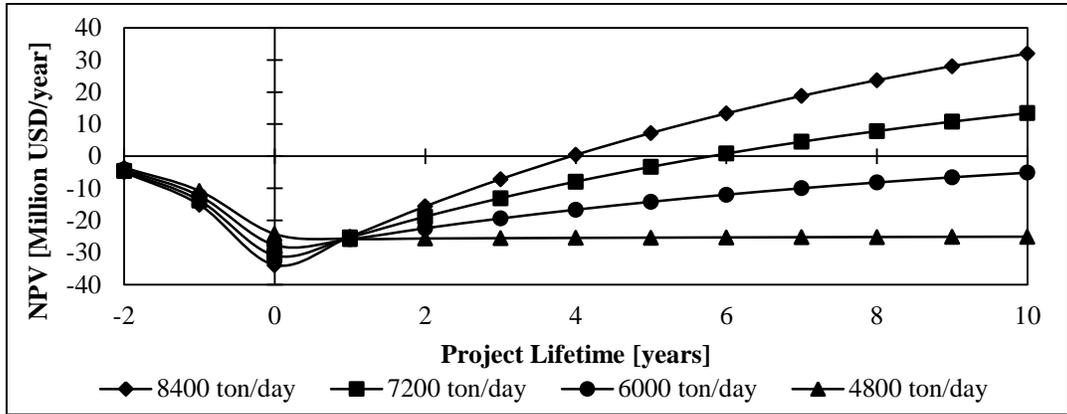
Fig. 5 Influence of process scale in NVP

In Fig 5 it can be observed that for the process scale under study (6000 tons/day) there are no process gains over the project lifetime. In contrast, a capital recovery (positive VPN) is observed for process scales of 7200 ton/day and 8400 ton/day with payback periods of 6 and 4 years, respectively. In addition, it should be noted that the evaluation of the NPV is influenced by the yields of the products and their production flows. Nevertheless, it can also be observed that when the flow of feedstock increases, the costs of fixed capital investment and working capital investment increase, due to the equipment size scale up. On the other hand, it is expected that the sale costs will be higher than the production costs for the feed flows that present profits from the process. In this sense, the ethanol cost in the market is 0.9 USD/kg which is higher than 0.88 USD/kg for a flow of feedstock of 8400 tons/day, and lower than 0.93 USD/kg for 4800 tons/day. The latter represent the extreme cases of scale analysis.

3.2.2   Comparison between biochemical and thermochemical for energy production using Pinus patula

Despite the fact that the production of ethanol using forest materials (in this case, *Pinus patula*) is economical feasible, most of this raw material is destined to the direct production of energy through incineration or gasification technologies. Therefore, below an energetic analysis is presented for both pathways based on the HHV of biomass and LHV of products. Using Eq. (3) and its corresponding parameters (VM=82.14 ; FC=17.64 ; ASH=0.23) [24], the HHV for *Pinus patula* is 20.08 MJ kg^{-1}. On the other hand, the LHV for energetic products are: 26.86 MJ kg^{-1} for ethanol [45] and 185.9 MJ kg^{-1} for gasification (H_2=1212.13 ; CH_4=501.59 ; CO=101.057 in MJ kg^{-1}) [46]. Then according to the results from the energy balance of both process, the energy yield of the ethanolic fermentation is lower than the gasification of *Pinus patula*, with values of 4.11 MJ/kg and 7.16 MJ/kg, respectively. As a result, the net energy efficiency of both processes is 23% for ethanol and 43% for syngas production. **Fig. 6** and **fig. 7** present the Sankey diagrams, which show in a graphical way the global energy balance of the process. The energy balance shows that outputs also represent the energy losses of the process. These amounts are referring to the energy in the inputs that is not converted into the respective product. The high amount of losses are associated to the high feed flow rate of feedstock, that can be minimize including more energetic products as more biofuels.
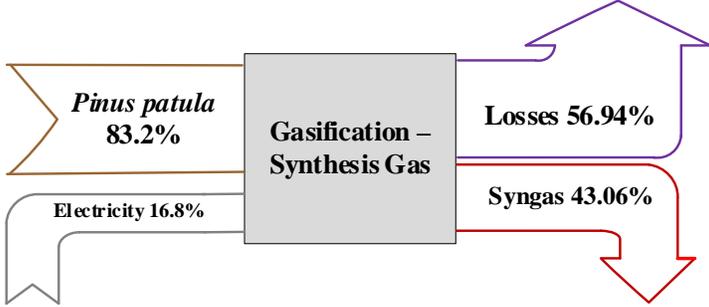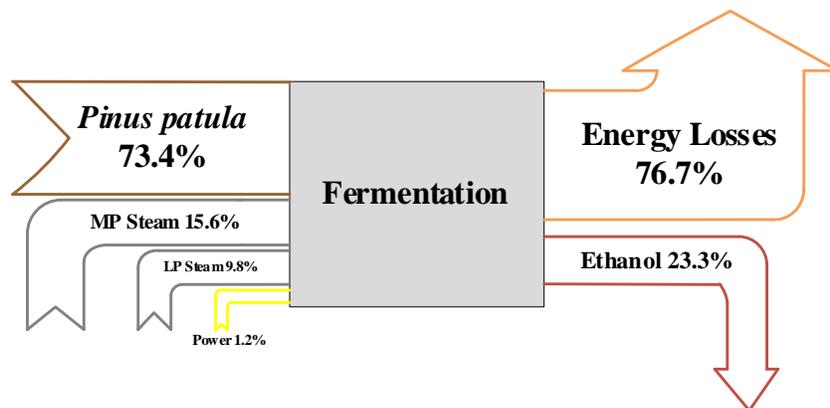

Fig. 6 Sankey diagram for gasification process

Fig. 7 Sankey diagram for fermentation process

Regardless the high pretreatment requirements of *Pinus patula* and the relative low energy efficiency, the production of ethanol through fermentation can improved the valorization of this raw material in comparison to the electricity generation. Electricity cannot be considered an added-value product due to the low market price and the diversity of methods to produce it, especially in Colombia where hydropower plants are used to produce more than 60% of the electricity [47]. On the other hand, the increment of the earth's temperature due to the global warming has increased the concern of using fossil fuels as energy carriers. It should be noted that the use of biofuels reduces greenhouse gas emissions compared to fossil fuels. Thus, for each kilogram of oil burned, 7.1 kg of CO2 is emitted, while for each kilogram of alcohol burned, 0.9 kg of CO_2 is emitted [48], [49] In this sense, ethanol is taking an important place as a future replacement of fossil fuels, especially in automobiles.

In order to keep the increment of the earth's temperature as low as possible, mixtures between fossil fuels and ethanol are used due to the reduction on the emissions from the combustion of these fuels. This scenario provides an opportunity not only to evaluate different technologies to produce energy but also to consider other raw materials that can be transformed in added-value products such as the ethanol.

4. CONCLUSION

In the experimental ethanol fermentation it was necessary concentrate the hydrolysate (13.5 g/L) due to low solids concentration in the enzymatic hydrolysis (15 g/L) and thus, to obtain a higher sugar concentration. However, it is possible to produce ethanol from *Pinus patula* with average experimental yield 0.35 g ethanol/g glucose. From the simulation procedure, the fermentative process of *Pinus patula* has proven for higher capacities (> 6000 ton per day) generating lower production costs, even lower than the market price. Consequently, the process can provide positive NPV values.

The energy analysis was focused in the comparison of the fermentation and gasification pathways for energy production. As a result, the net energy efficiency of both processes was 18% and 35%, respectively. Therefore, electricity from gasification cannot be considered an added-value product due to the low market price and the diversity of methods to produce it, especially in Colombia. Additionally ethanol reduces the impacts of climate change by contributing to the control of air pollution, guaranteeing energy security, promoting local development and providing independence from fluctuations in the market situation and supply of oil.

5. ACKNOWLEDGEMENTS

REFERENCES

[1]   V. Hernández, J. M. Romero-García, J. A. Dávila, E. Castro, and C. A. Cardona, "Techno-economic and environmental assessment of an olive stone based biorefinery," *Resour. Conserv. Recycl.*, vol. 92, pp. 145–150, 2014.

[2]   A. dos S. Polidoro *et al.*, "Valorization of coffee silverskin industrial waste by pyrolysis: From optimization of bio-oil production to chemical characterization by GC × GC/qMS," *J. Anal. Appl. Pyrolysis*, vol. 129, no. August 2017, pp. 43–52, 2017.

[3]   B. Janissen and T. Huynh, "Chemical composition and value-adding applications of coffee industry by-products: A review," *Resour. Conserv. Recycl.*, vol. 128, no. September 2017, pp. 110–117, 2018.

[4]   D. Barjolle, X. F. Quiñones-Ruiz, M. Bagal, and H. Comoé, "The Role of the State for Geographical Indications of Coffee: Case Studies from Colombia and Kenya," *World Dev.*, vol. 98, pp. 105–119, 2017.

[5]   J. Andres Quintero *et al.*, "Social and techno-economical analysis of biodiesel production in Peru," *Energy Policy*, vol. 43, pp. 427–435, 2012.

[6]   S. H. Mohd Azhar *et al.*, "Yeasts in sustainable bioethanol production: A review," *Biochem. Biophys. Reports*, vol. 10, no. March, pp. 52–61, 2017.

[7]   ECOPETROL, "Biocombustibles - Gestión ambiental proactiva," Cartagena, 2014.

[8]   B. Herrera Jaime, S. Leyva Rolon, V. Ortiz Ceron, J. F. Cardenas Valderrama, and E. Garzon Lozano, "Biocombustibles en Colombia," Bogotá, 2009.

[9]   C. A. García, R. Betancourt, and C. A. Cardona, "Stand-alone and biorefinery pathways to produce hydrogen through gasification and dark fermentation using Pinus Patula," *J. Environ. Manage.*, vol. 203, pp. 695–703, 2017.

[10]   M. et al. Ospina, "Guías silviculturales para el manejo de especies forestales com miras a la producción de madera en la zona andina Colombiana. El pino pátula," 2011.

[11]   ProExport, "Sector Forestal en Colombia," 2012.

[12]   S. I. Mussatto, J. Moncada, I. C. Roberto, and C. A. Cardona, "Techno-economic analysis for brewer's spent grains use on a biorefinery concept: The Brazilian case," *Bioresour. Technol.*, vol. 148, pp. 302–310, 2013.

[13]   J. L. Stephen and B. Periyasamy, "Innovative developments in biofuels production from organic waste materials: A review," *Fuel*, vol. 214, no. September 2017, pp. 623–633, 2018.

[14]   A. H. Sebayang *et al.*, "Prediction of engine performance and emissions with Manihot glaziovii bioethanol − Gasoline blended using extreme learning machine," *Fuel*, vol. 210, no. September, pp. 914–921, 2017.

[15]   C. Dong, Y. Wang, H. Zhang, and S. Y. Leu, "Feasibility of high-concentration cellulosic bioethanol production from undetoxified whole Monterey pine slurry," *Bioresour. Technol.*, vol. 250, no. October 2017, pp. 102–109, 2018.

[16]   M. Lee, S. Cho, and J. Kim, "A comprehensive model for design and analysis of bioethanol production and supply strategies from lignocellulosic biomass," *Renew. Energy*, vol. 112, pp. 247–259, 2017.

[17]   X. Liu, M. Lu, N. Ai, F. Yu, and J. Ji, "Kinetic model analysis of dilute sulfuric acid-catalyzed hemicellulose hydrolysis in sweet sorghum bagasse for xylose production," *Ind. Crops Prod.*, vol. 38, no. 1, pp. 81–86, 2012.

[18]   X. Zhao, R. Wu, and D. Liu, "Production of pulp, ethanol and lignin from sugarcane bagasse by alkali-peracetic acid delignification," *Biomass and Bioenergy*, vol. 35, no. 7, pp. 2874–2882, 2011.

[19]   L. L. G. Fuentes, S. C. Rabelo, R. M. Filho, and A. C. Costa, "Kinetics of lime pretreatment of sugarcane bagasse to enhance enzymatic hydrolysis," *Appl. Biochem. Biotechnol.*, vol. 163, no. 5, pp. 612–625, 2011.

[20]   J. Moncada, C. A. Cardona, J. C. Higuita, J. J. Velez, and F. E. Lopez-Suarez, "Wood residue (Pinus

patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments," *Chem. Eng. Sci.*, vol. 140, pp. 309–318, 2016.

[21] J. A. Quintero and C. A. Cardona, "Process Simulation of Fuel Ethanol Production from Lignocellulosics using Aspen Plus," *Ind. Eng. Chem. Res.*, vol. 50, no. 10, pp. 6205–6212, May 2011.

[22] A. A. P. Susastriawan, H. Saptoadi, and Purnomo, "Small-scale downdraft gasifiers for biomass gasification: A review," *Renew. Sustain. Energy Rev.*, vol. 76, no. February, pp. 989–1003, 2017.

[23] J. J. Hernández, M. Lapuerta, and E. Monedero, "Characterisation of residual char from biomass gasification: effect of the gasifier operating conditions," *J. Clean. Prod.*, vol. 138, pp. 83–93, 2016.

[24] C. A. García Velásquez, "Hydrogen production through gasification and dark fermentation," National University of Colombia at Manizales, 2016.

[25] Q. Jin, H. Zhang, L. Yan, L. Qu, and H. Huang, "Kinetic characterization for hemicellulose hydrolysis of corn stover in a dilute acid cycle spray flow-through reactor at moderate conditions," *Biomass and Bioenergy*, vol. 35, no. 10, pp. 4158–4164, 2011.

[26] M. Selig, N. Weiss, and Y. Ji, "Enzymatic Saccharification of Lignocellulosic Biomass," *Natl. Renew. Energy Lab.*, no. March, pp. 1–5, 2008.

[27] G. L. Miller, "Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar," *Anal. Chem.*, vol. 31, no. 3, pp. 426–428, 1959.

[28] J. A. López, V. M. Trejos, and C. A. Cardona, "Parameters estimation and VLE calculation in asymmetric binary mixtures containing carbon dioxide + n-alkanols," *Fluid Phase Equilib.*, vol. 275, no. 1, pp. 1–7, 2009.

[29] J. A. Quintero, J. Moncada, and C. A. Cardona, "Techno-economic analysis of bioethanol production from lignocellulosic residues in Colombia: A process simulation approach," *Bioresour. Technol.*, vol. 139, pp. 300–307, 2013.

[30] J. R. Kwiatkowski, A. J. McAloon, F. Taylor, and D. B. Johnston, "Modeling the process and costs of fuel ethanol production by the corn dry-grind process," *Ind. Crops Prod.*, vol. 23, no. 3, pp. 288–296, May 2006.

[31] J. A. Quintero and C. A. Cardona, "Ethanol dehydration by adsorption with starchy and cellulosic materials," *Ind. Eng. Chem. Res.*, vol. 48, no. 14, pp. 6783–6788, 2009.

[32] M. Peters, K. Timmerhaus, and R. West, *Plant Design and Economics for Chemical Engineers*, Fifth ed. New York, 2003.

[33] "Federación Nacional de Biocombustibles de Colombia." [Online]. Available: http://www.fedebiocombustibles.com/v3/estadistica-precios-titulo-Alcohol_Carburante_(Etanol).htm. [Accessed: 30-Mar-2018].

[34] M. S. Peters, K. D. Timmerhaus, and R. E. West, *Materials Transfer, Handling, and Treatment Equipment-Design and Costs*. 2004.

[35] C. A. García, J. Moncada, V. Aristizábal, and C. A. Cardona, "Techno-economic and energetic assessment of hydrogen production through gasification in the Colombian context: Coffee Cut-Stems case," *Int. J. Hydrogen Energy*, vol. 42, no. 9, pp. 5849–5864, 2017.

[36] M. Puig-Arnavat, J. C. Bruno, and A. Coronas, "Review and analysis of biomass gasification models," *Renew. Sustain. Energy Rev.*, vol. 14, no. 9, pp. 2841–2851, Dec. 2010.

[37] R. Rauch, J. Hrbek, and H. Hofbauer, "Biomass gasification for synthesis gas production and applications of the syngas," *Wiley Interdiscip. Rev. Energy Environ.*, vol. 3, no. 4, pp. 343–362, Jul. 2014.

[38] M. Puig-Arnavat, J. C. Bruno, and A. Coronas, "Review and analysis of biomass gasification models," *Renew. Sustain. Energy Rev.*, vol. 14, no. 9, pp. 2841–2851, Dec. 2010.

[39] L. E. Rincón, L. A. Becerra, J. Moncada, and C. A. Cardona, "Techno-economic analysis of the use of fired cogeneration systems based on sugar cane bagasse in south eastern and mid-western regions of Mexico," *Waste and Biomass Valorization*, 2014.

[40] D. R. Nhuchhen and P. Abdul Salam, "Estimation of higher heating value of biomass from proximate analysis: A new approach," *Fuel*, vol. 99, pp. 55–63, 2012.

[41] Nyangi Chacha, "Comparison of Escherichia coli KO11 and Saccharomyces cerevisiae ATCC 96581 in fermenting Pinus patula hydrolysate pretreated at different steam explosion severity," *African J. Biotechnol.*, vol. 11, no. 37, 2012.

[42] G. M. Hawkins and J. Doran-Peterson, "A strain of Saccharomyces cerevisiae evolved for fermentation of lignocellulosic biomass displays improved growth and fermentative ability in high solids concentrations and in the presence of inhibitory compounds," *Biotechnol. Biofuels*, vol. 4, no.

1, p. 49, 2011.

[43] Q. A. Nguyen, M. P. Tucker, F. A. Keller, D. A. Beaty, K. M. Connors, and F. P. Eddy, "Dilute acid hydrolysis of softwoods," *Appl. Biochem. Biotechnol.*, 1999.

[44] M. Qian, S. Tian, X. Li, J. Zhang, Y. Pan, and X. Yang, "Ethanol production from dilute-acid softwood hydrolysate by co-culture," *Appl. Biochem. Biotechnol.*, 2006.

[45] C. E. Wyman and N. D. Hinman, "Ethanol - Fundamentals of production from renewable feedstocks and use as a transportation fuel," *Appl. Biochem. Biotechnol.*, 1990.

[46] T. Waldheim, L. Nilsson, "Heating value of gases from biomass gasification," 2001.

[47] U. de P. E. (UPME), "Informe Mensual De Variables De Generación Y Del Mercado Eléctrico Colombiano," Bogotá, Colombia, 2015.

[48] M. Ishida, D. Zheng, and T. Akehata, "Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis," *Energy*, vol. 12, no. 2, pp. 147–154, Feb. 1987.

[49] H. Hondo, "Life cycle GHG emission analysis of power generation systems: Japanese case," *Energy*, vol. 30, no. 11–12, pp. 2042–2056, Aug. 2005.