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Hydrogen production by gasification and dark fermentation from woody wastes: Energy and Environmental Analysis.

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Abstract

New efforts in the search of alternative clean and renewable energy to replace the current energy precursors 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 value-added 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 using Aspen Plus v8.0 for the production of hydrogen through gasification and dark fermentation. In order to feedback the simulation step, verification experiments were developed at small scale using "GEK Gasifier (10 KW/h) Power Pallet". The results demonstrated that the scale of the production and the separation of byproducts define the best technologies or ways to be used to produce bioenergy in this case.

Keywords

Hydrogen, lignocellulosic biomass, bioenergy, sustainability

1. Introduction

The increasing global energy demand based mainly on fossil fuels, rural development requirements and the environmental concerns as for example greenhouse gases have increased interest in the search for new forms of renewable energy. Colombia is a country of high agricultural production, however, the principal source of energy is oil which contributes up to 40% of the primary energy generation [1]. In last years, Colombia has been promoting the use of wastes especially from the agribusiness processes to obtain high-value products (i.e, cogeneration processes to obtain electricity from sugarcane bagasse [2]). However, lack of energy policies in Colombia has hindered the implementation of new technologies for the proper use of this waste.

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 Mining and Energy Planning Unit (UPME), Colombia has about 2,395,000 hectares with natural and planted forests from which about 1,941,135 tons/year of wood residues are obtained [3]. Assortment of wood residues and transportation logistics are the main problems for its use as energy source in bioenergy production. Due to these problems, woody materials have been used in combustion process for cooking and heating water where the energy efficiency is very low.

The high dependence on fossil fuels of the main economic sectors in Colombia highlights the necessity of implementing new technologies to produce high-impact products with high energy potential taking advantage of the large amount of wastes generated at different stages of the agribusiness supply chain. Thermochemical processes (i.e, gasification) have been gaining importance due to it allows an extensive range of biomass and its high productivity. On the other hand, biochemical processes such as dark fermentation require more research for its implementation, however it can be an alternative for bioenergy production with low energy consumption [4].

Hydrogen is nowadays a promising source of energy that can be used directly and indirectly as storage fuel with less environmental issues, especially without CO_2 emissions [5]. 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 much lesser [6][7]. Several authors have studied the influence of operating parameters in biomass gasification and dark fermentation for hydrogen production [8]–[10], [11]–[13].

The aim of this work is to develop a techno-economic, energy and environmental assessment for hydrogen production through gasification and dark fermentation using Pinus Patula as energy source. Techno-economic evaluation was performed considering different scenarios for gasification and dark fermentation in order to compare them in terms of profitability. Energy and environmental assessment were developed in order to evaluate the process energy efficiency and emissions, respectively.

2. Methods

2.1 Process Description

2.1.1 Gasification

Gasification consist 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 air, water or oxygen as gasifying agent. Gasification process can be divided in three stages: Raw material pretreatment, chemical reactions involving biomass gasification and hydrogen purification. Particle size and moisture content are the key parameters in the pretreatment stage due to hydrogen content in the syngas and process performance of the gasification can depending on the before mentioned parameters. Zainal., et al [14] evaluated the effect of moisture content in the biomass related to the hydrogen content and calorific value of the generated gas in a downdraft gasifier. High moisture content increases hydrogen production but the calorific value of the gas decreases. Small particles have larger surface area and therefore faster heating rate, for this reason it can be expected that the particle size affect the product gas composition [15]. In this study, a particle size of 1-2 cm and a moisture content of 20% were selected.

The second stage is related to the reactions involved inside the gasifier. Chemical pathway of gasification can be divided 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 CO_2, CO, H_2 and H_2O. The char produced in the pyrolysis and the combustion zone goes into the reduction zone where char gasification takes place to produce CO_2, CO, H_2 and CH_4. Ash and the remaining char are separated from the syngas using a cyclone. In order to improve hydrogen content in the generated gas, a catalyst adsorption was proposed. Carbonation reaction is based on the conversion of carbon dioxide (CO_2) into calcium carbonate ($CaCO_3$) using calcium oxide (CaO) as catalyst. Nikulshima et al., [16] studied the effect of CaO based catalyst in a thermochemical cycle to capture CO_2 from air concentrating solar energy.

Finally, high purity hydrogen can be obtained using a metallic membrane separating the hydrogen from the generated syngas. Ockwig et al., [17] described a complete review of different type of membranes for hydrogen separation. Figure 1 shows the process scheme for biomass gasification.

Figure 1. Gasification Scheme

2.1.2 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 [12]. Due to high cellulose crystallinity and low biodegradability, lignocellulosic biomass may require a pretreatment prior to biohydrogen fermentation [13]. For this reason, a mild-acid treatment and enzymatic hydrolysis of cellulose are proposed. Acid hydrolysis under mild conditions is the main process used for saccharification of lignocellulosic biomass. Additionally, for this study, sulfuric acid (6%w/w) at 130°C was used to obtain xylose as second carbon source for dark fermentation. One problem associated with the dilute-acid hydrolysis is the formation of toxic compounds such as phenolic compounds. For this reason, detoxification is proposed as an alternative to convert these compounds into others less toxic that may not inhibit the cell growth. $Ca(OH)_2$ alkaline treatment is widely used in hydrolyzates detoxification [18]. The cellulose unconverted fraction from the acid hydrolysis can be degraded to produce glucose by enzymatic saccharification. Two types of enzymes (Cellulase and β-glucosidase) at 50°C were used in this process.

The pretreated glucose and xylose obtained from the enzymatic and acid hydrolysis can be used as carbon source for hydrogen production by the moderate thermophile *Thermoanaerobacterium thermosaccharolyticum*. From this process, hydrogen, carbon dioxide and other metabolites (ethanol, acetic acid, butyric acid, among others) are obtained. Furthermore, the separation of the ethanol as main byproduct was considered. As mentioned in section 2.1.1, the separation of hydrogen and carbon dioxide using a membrane was proposed. Figure 2 shows the proposed dark fermentation scheme.

Figure 2. Dark Fermentation Scheme

2.2 Process scenarios

Different scenarios for gasification and dark fermentation were proposed in order to evaluate productivity, profitability and environment impact taking into account hydrogen as main product of these process configurations. Table 1 shows the process schemes proposed for this study. Three scenarios for gasification were performed taking as main products electricity generation, hydrogen and ethanol production. Two scenarios for dark fermentation in terms of hydrogen and ethanol production were evaluated.

Table 1. Scenarios proposed for hydrogen production

Scenario 1 considers only the production of hydrogen through gasification. Other two scenarios are proposed considering the production of ethanol and electricity. Scenarios 2 considers the use of 50% of the syngas produced in the gasification for hydrogen production and the remaining 50% for the generation of electricity using the syngas as fuel for a gas engine. Meanwhile, Scenario 3 considers the ethanol production from a fraction (30%) of the Pinus Patula used 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.

For dark fermentation, two scenarios are proposed. The first scenario considers only the production of hydrogen; meanwhile, the second scenario considers the separation of the principal byproduct from the fermentation broth, in this case ethanol.

2.3 Simulation procedure

For all proposed scenarios, mass and energy balances were obtained using simulation procedures. The software use 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 profile using kinetic models used in the simulation procedure was performed in software packages such as Matlab. Hydrogen production through air gasification was developed using equilibrium reactions reported by Dejtrakulwong et al., [9]. Carbonation and calcination reactions were calculated using the kinetic law reported by Nikulshina et al., [16]. Fermentation using *S. cerevisae* for ethanol production was calculated using the kinetic model reported by Rivera et al., [19]. Dark fermentation for hydrogen production was modeled using a Monod kinetic model reported by Ren et al., [20]. For simulation purposes, the non-random two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden-O´Connell equation of state was applied for description of the vapor phase. Additional data such as physical properties was obtained from the work of Wooley and Putsche [21].

2.4 Energy Analysis

From the simulation procedure, the energy needs of the process was obtained. The simulation results were used to determine the amount of energy required for each scenario to transform the Pinus Patula into bioenergy products. However, the analysis of the amount of energy contained in the raw material that is transformed into hydrogen, ethanol or electricity in terms of heating values was performed in order to evaluate the process efficiencies.

Energy content of feedstock and the bioenergy products (hydrogen, ethanol and syngas) can be analyzed in terms of the heating value of the components. The higher heating value (HHV) of biomass fuels on dry basis can be calculated as function of the proximate analysis [22]. The energy content of the gas generated depends on the concentration of CO, H_2 and CH_4. Meanwhile, the HHV of ethanol was obtained from data reported by the National Institute of Standards and Technology (NIST) [23].

2.5 Economic Evaluation

A basic equipment mapping adapted to the economic conditions in Colombia was developed to determine the operating costs of the scenarios proposed including the raw materials, utilities, labor and maintenance, general plant and administrative costs. Mass and energy balances obtained from the simulation procedure were used in the software Aspen Economic Analyzer to evaluate the economic assessment of all proposed scenarios. The profit margin was calculated based on the operating costs and the process productivity for each bioenergy product. Table 2 shows the prices of utilities, raw materials and products used in the economic evaluation.

2.6 Environmental Evaluation

The impacts that the process would generate into the environment can be calculated using the Waste Reduction Algorithm (WAR), developed by the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency (EPA). The software evaluates the process in terms of the potential environment impacts (PEI) which are related to the effect that the material and energy balance would have on the environment if they were to be emitted into the environment [24]. War Algorithm evaluates the PEI in terms of eight categories: Human toxicity by ingestion (HTPI), human toxicity by dermal exposition or inhalation (HTPE), aquatic toxicity potential (ATP), Global warming (GWP), Ozone depletion potential (ODP), Photochemical oxidation potential (PCOP) and acidification Potential (AP).

Table 2. Utilities, raw materials and products prices

3. Results

In order to validate the simulation results, experimental data from gasification of Pinus Patula in a downdraft gasifier using air as gasifying agent was used. Table 3 and 4 show some characteristics of the Pinus Patula and the experimental data used in the simulation part, respectively. Elemental analysis and the lower heating value (LHV) were calculated based on theoretical correlations from the chemical composition and proximate analysis [22].

From table 4, it can be noticed that the combined percentage of hydrogen and carbon monoxide content (which are responsible for the calorific value of fuel) after simulation is 38.82%, against an experimental value of 32.57%. A non-total agreement can be observed in the heating value predicted (4.558 MJ/Nm^3) in comparison with the experimental value (5.551 MJ/Nm^3). Methane is another of the species that contributes to the heating value calculation; however, the methane content in the simulation approach is lower than that of the experimental part. Thus, the predicted calorific value of the gas is lower.

Table 3. Characterization of Pinus Patula.

3.1 Process Simulation

From all simulated scenarios, the mass and energy balances are obtained to evaluate the production capacities and yields from each process as shown in table 5. Scenarios 2 and 3 use a fraction of the syngas for electricity generation and scenario 3 used a fraction of the Pinus Patula for ethanol production. The results obtained for this evaluation can be shown in table 6.

Table 4. Experimental parameters used in the simulation.

Table 5. Production capacities and yields of the evaluated cases.

Table 6. Electricity generation

Hydrogen production rate is higher in scenario 1 due to all the syngas produced in the gasification is used as raw material for hydrogen production in contrast to scenarios 2 and 3. However, scenarios 2 and 3 has higher hydrogen rate compared to scenarios 4 and 5 using dark fermentation. Additionally, scenarios 2 and 3 generate electricity using the remaining part of the syngas produced in the gasification. In scenario 3 a fraction of the Pinus Patula is used to produce ethanol through fermentation; thus the amount of electricity generated in the scenario 2 is higher, as can be observed in table 6.

The ethanol productivity in scenario 3 is higher than that obtained in the scenario 5. The principal reason of this behavior is related to the fact that the ethanol obtained in the dark fermentation process is separated of the fermentation broth as a byproduct of the process, meanwhile in scenario 3 the main objective of the fermentation is the ethanol production.

3.2 Energy Analysis

Figure 3 shows the energy consumption of the process as function of the biomass conversion. Scenarios 1, 2 and 3 has a similar energy consumption due to the distribution of the mass balance in the process, mainly in the syngas used for hydrogen production. Scenario 1 has the higher energy consumption given the use of all the syngas to produce hydrogen, and hydrogen purification of this process has high energy requirements. In the dark fermentation scenarios, the ethanol separation (scenario 5) from the fermentation broth requires high amounts of energy.

Figure 3. Energy consumption of the scenarios proposed.

Even if the process energy consumption is relative similar, scenarios 2 and 3 have different bioenergy products (i.e ethanol and electricity) that improve the global efficiency of the process as shown in figure 4. Energy efficiency is defined as the ratio of energy content in the products and the total energy content of feedstock [26]. Scenario 3 has the higher process efficiency due to the production of hydrogen, electricity and ethanol. Biochemical processes have low productivity due to batch regime operation; thus, the process efficiency of the scenarios 4 and 5 are relative low compared to those of gasification scenarios.

Figure 4. Scenarios Efficiency

3.3 Economic Evaluation

Table 7 shows the contribution of each economic parameter in the production cost of each of the bioenergy products. The hydrogen production cost in scenarios 1, 2 and 3 are among the production cost for gasification reported by Parthasarathy et al., [5]. Nevertheless, these production costs through this technology remain higher compared to other existing technologies for hydrogen production such as steam methane reforming (SMR), in which the production cost is 0.75 USD/Kg. For scenarios 4 and 5, the production costs are very high; however it should be noted that the separation of ethanol as byproduct of the dark fermentation improves this cost.

According to the National Federation of Biofuels in Colombia (Fedebiocombustibles), the fuel ethanol sale price is around 0.72 USD/liter [27]. However, the production cost calculated of ethanol for scenarios 3 and 5 is higher than its sale price in Colombia. Production scale is the determining factor for the economic viability of such processes [28]. On the other hand, the production cost of electricity through gasification is lower compared to the sale price in Colombia (see Table 2).

From table 7, it can be noted that the parameters that have major contribution to the hydrogen production cost are the utilities followed by the raw materials costs. In scenarios 1, 2 and 3, the principal contribution is related to the utilities cost due to the high energy needs in the hydrogen purification. Whereas, the raw materials cost is the parameter that has the major contribution in the hydrogen production cost for scenarios 4 and 5. The high raw materials cost is due mainly to the inputs used in the pretreatment stage (see section 2.1.2). This behavior can be observed more clearly in Figure 5.

Table 7. Economic evaluation of the principal bioenergy products.

Figure 5. Parameters contribution in the hydrogen production cost.

Figure 6. Profit margin of hydrogen production

According to the above, a comparison between the sale price and the production cost was applied to evaluate the profit margin of the processes. Figure 6 shows the profit margin of hydrogen production for the evaluated scenarios. Scenario 1 has the higher profit margin due to the use of all the syngas in the hydrogen production; however scenarios 2 and 3 has similar profit margin values and they have the advantage of producing ethanol and electricity that can enhance the profitability of the process. For scenarios 4 and 5, it can be noted that the separation of ethanol can improve the hydrogen production cost due to the valorization of this byproduct, which results in reducing the costs involved in the hydrogen production as can be observed in table 7.

3.4 Environmental Evaluation

The environmental impact calculation is based on the mass and energy balances obtained from the simulation. According to this, figures 7, 8 and 9 are presented taking into account the environmental impact as function of different products. Figure 7 shows the environmental impact evaluation based on hydrogen as only product in all scenarios. Figure 8 shows this evaluation taking into account hydrogen and ethanol as only products and finally, the behavior of all scenarios with their corresponding products is shown in figure 9.

In figure 7, hydrogen is considered as only product for all scenarios; thus, ethanol and electricity were taken as outputs emitted directly into the environment. According to this, the PEI increases progressively in all scenarios related to the high amount of wastes emitted especially in the dark fermentation. Ethanol is one of the products obtained in the scenarios 3 and 5; the valorization of this product markedly decreases the environmental potential impact in these scenarios, as it can be observed in figure 8. Figure 9 shows the behavior of the scenarios if we consider all the products obtained (hydrogen, ethanol and electricity). As can be observed in figure 9, the PEI generated by gasification processes (scenarios 1, 2 and 3) are very low due to the correct exploitation of all process streams. Whereas, dark fermentation (scenarios 4 and 5) has high PEI related to contamination by secondary metabolites presented in the fermentation broth such as acetic acid, butyric, among others. The results suggest that the friendliest configurations are the gasification scenarios followed by the dark fermentation with ethanol as by product.

Figure 7. Environmental evaluation with hydrogen as main product.

Figure 8. Environmental evaluation with hydrogen and ethanol as main products.

Figure 9. Environmental evaluation with hydrogen, ethanol and electricity as main products.

4. Conclusions

Thermochemical processes have higher energy requirements in comparison to biochemical processes. Nevertheless, the process efficiency is higher due to the exploitation of a large variety of byproducts obtained from the hydrogen production. These high results are reflected in the hydrogen production cost, which is low but still requires more improvement in order to compete with mature technologies such as steam methane reformer (SRM). Biochemical processes require more research not only in terms of productivity but also in the proper use of metabolites in the fermentation broth. Acetic and butyric acid are products with a wide market demand; therefore their separation could improve the hydrogen production cost and reduce the emissions related to their final disposal.

5. Acknowledgments

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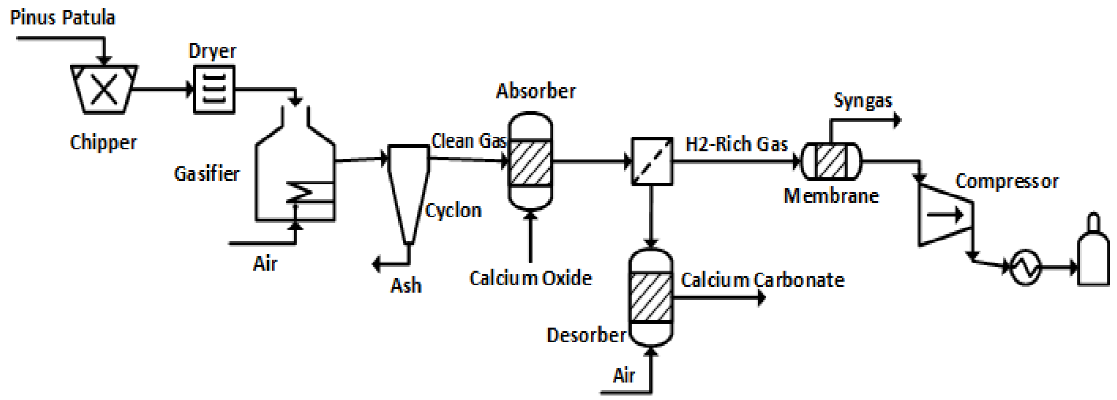

Figure 1. Gasification Scheme

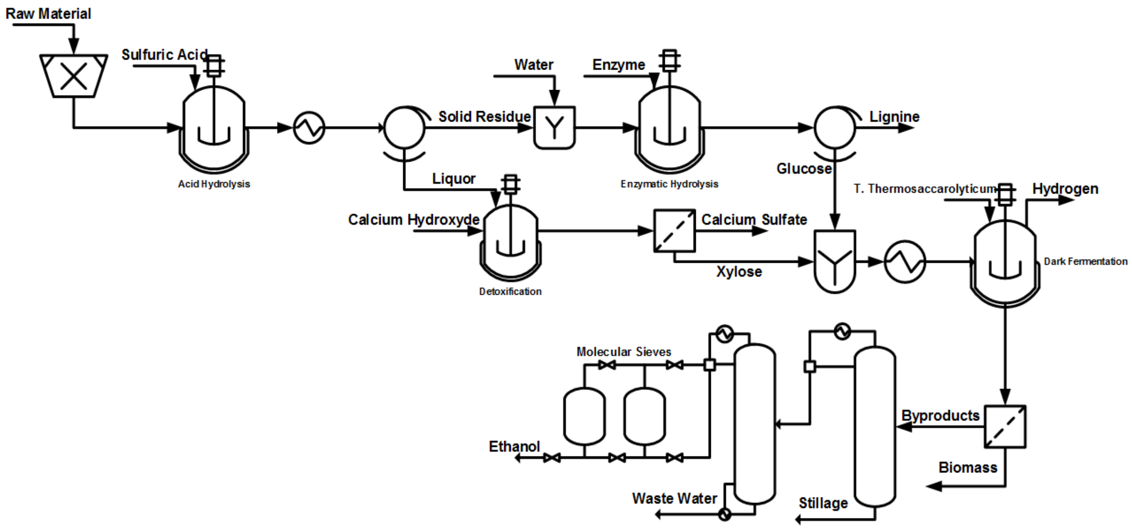

Figure 2. Dark Fermentation Scheme

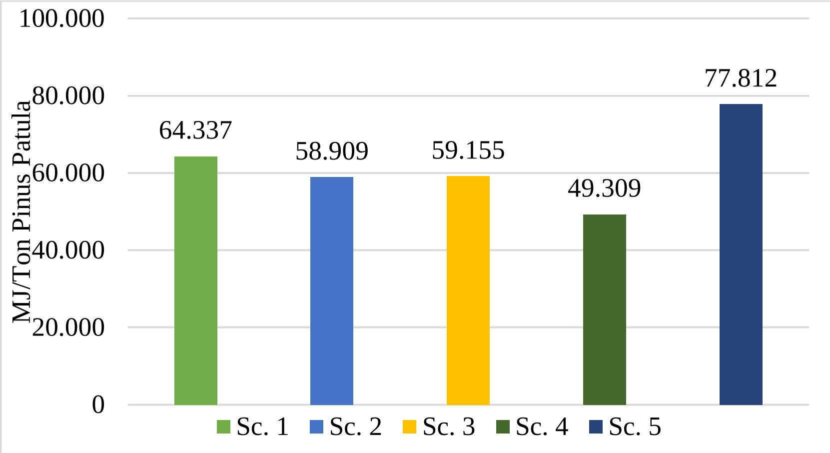

Figure 3. Energy consumption of the scenarios proposed.

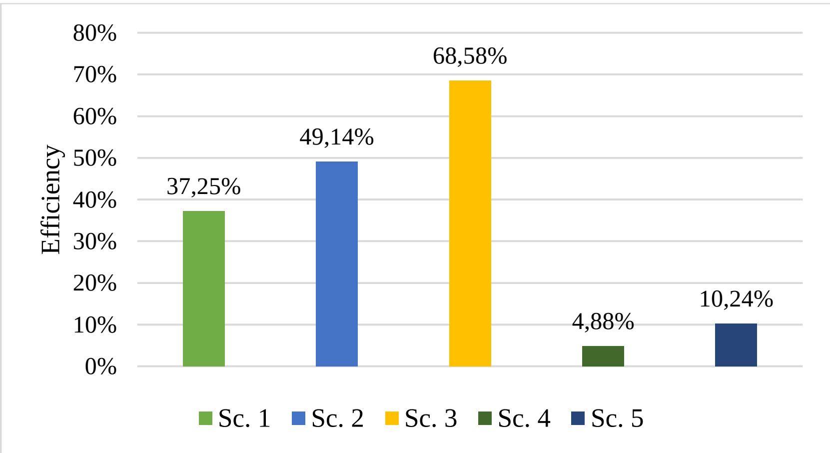

Figure 4. Scenarios Efficiency

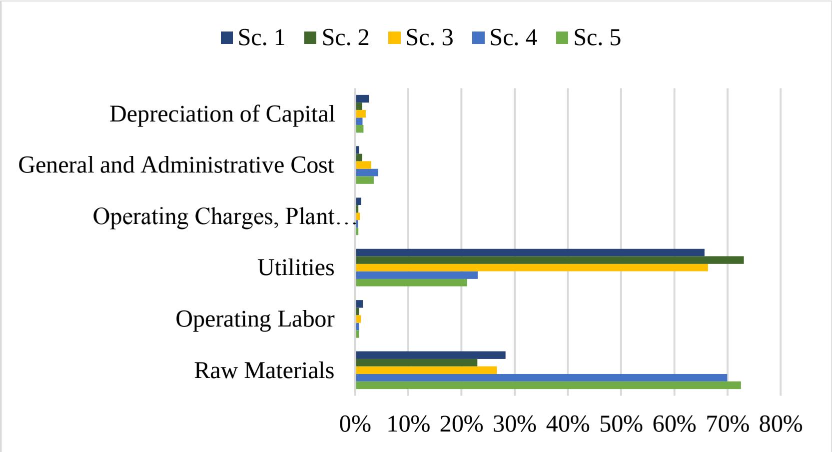

Figure 5. Parameters contribution in the hydrogen production cost.

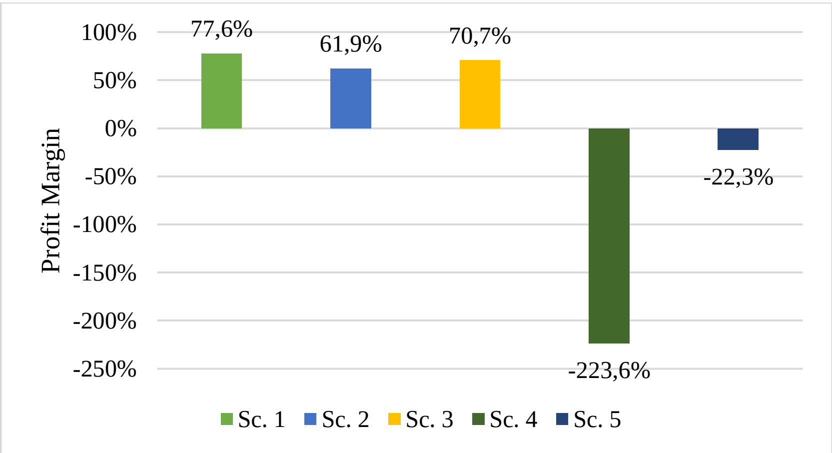

Figure 6. Profit margin of hydrogen production

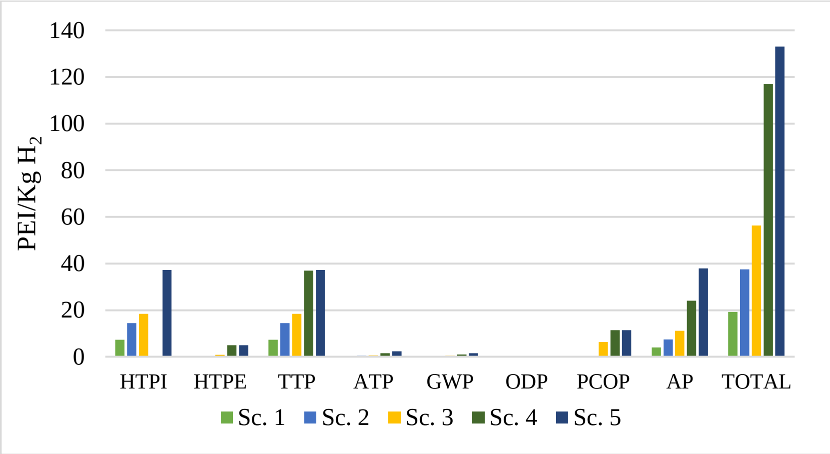

Figure 7. Environmental evaluation with hydrogen as main product.

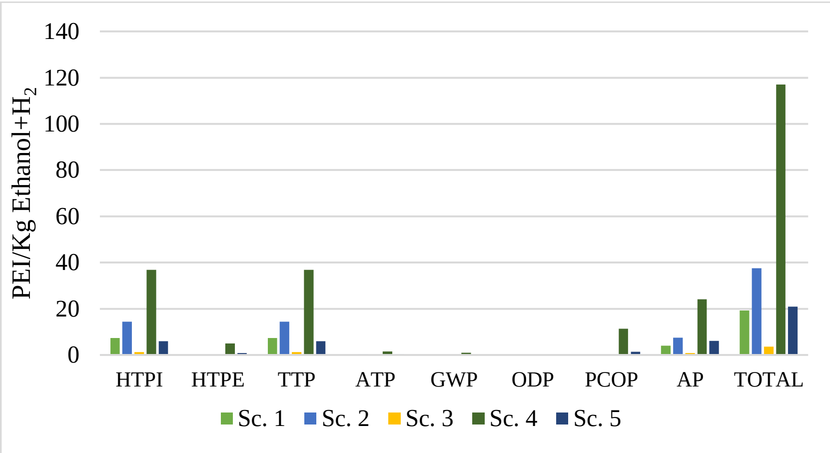

Figure 8. Environmental evaluation with hydrogen and ethanol as main products.

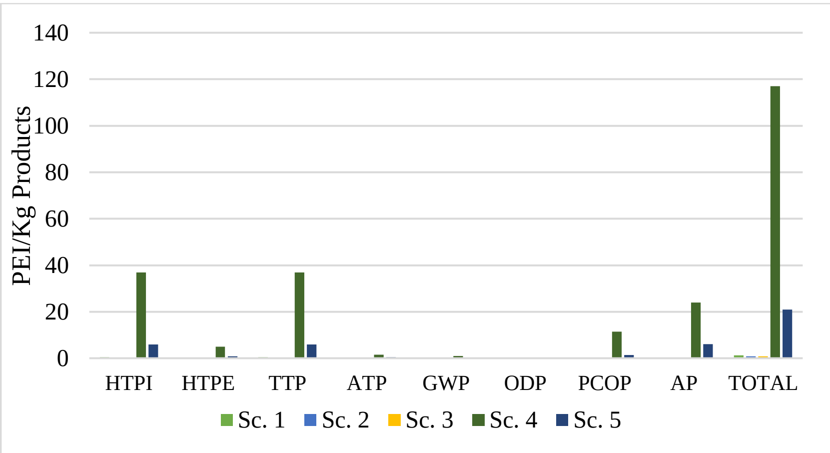

Figure 9. Environmental evaluation with hydrogen, ethanol and electricity as main products.

Table 1. Scenarios proposed for hydrogen production

Scenarios	Technology	Description
Scenario 1		Hydrogen
Scenario 2	Gasification	Hydrogen + Electricity
Scenario 3		Hydrogen + Electricity + Ethanol
Scenario 4	Dark Fermentation	Hydrogen
Scenario 5		Hydrogen + Ethanol

Table 2. Utilities, raw materials and products prices

Component	Price	Units
Pinus Patula	0.02[a]	USD/Kg
Sulfuric Acid	0.1	USD/Kg
Sodium Hydroxide	0.35	USD/Kg
Calcium Hydroxide	0.05	USD/Kg
Calcium Oxide	0.062	USD/Kg
Fuel Ethanol	1.24	USD/L
Hydrogen	14.05[b]	USD/Kg
Water	1.252	USD/m^3
Electricity	0.1	USD/kWh
High P. Steam (105 bar)	9.86	USD/ton
Mid P. Steam (30 bar)	8.18	USD/ton
Low P. Steam (3 bar)	1.57	USD/ton

[a] Price based on the statistics of plantain forest residue obtained from UPME [3].
[b] Based on hydrogen price projections for 2015 [25].

Table 3. Characterization of Pinus Patula.

Moisture Content (%wt)	9.52
Chemical Composition (%wt dry)	
Cellulose	35.66
Hemicellulose	29.69
Lignin	20.73
Extractives	13.66
Ash	0.25
Proximate Analysis (%wt dry)	
Volatile Matter	68.73
Fixed Carbon	30.98
Ash	0.28
Elemental Analysis (%wt dry)	
Carbon	51.26
Hydrogen	5.95
Oxygen	42.76
LHV (MJ/Kg)	19.1

Table 4. Experimental parameters used in the simulation.

Feedstock	**value**	**unit**
Particle Size	1-2	cm
Moisture Content	10-20	%wt
Downdraft Gasifier		
Temperature	800	°C
Air/Biomass Ratio	0.25	Kg Air/kg Biomass
Gas Composition (%Vol)	**Experimental**	**Simulation**
Hydrogen	16.87	19.69
Carbon Monoxide	15.7	19.13
Carbon Dioxide	10.75	12.63
Methane	2.56	0.005
Nitrogen	54.12	48.54
LHV (MJ/Nm^3)	5.551	4.558

Table 5. Production capacities and yields of the evaluated cases.

Scenarios	**Production**[a]		**Yields**[a]	
	Value	**Units**	**Value**	**Units**
Scenario 1	6.71	Ton H_2/day	0.059	Ton H_2/ton wood
Scenario 2	3.35	Ton H_2/day	0.03	Ton H_2/ton wood
Scenario 3	2.24	Ton H_2/day	0.02	Ton H_2/ton wood
	35,980	Liters Ethanol/day	318.2	Liters Ethanol/ton wood
Scenario 4	0.78	Ton H_2/day	0.007	Ton H_2/ton wood
Scenario 5[b]	5582.7	Liters Ethanol/day	49.4	Liters Ethanol/ton wood

[a] Calculated for 113.1 Ton of Pinus Patula/day

[b] Hydrogen productivity is the same for scenario 4

Table 6. Electricity generation

Scenarios	**Electricity (MW)**
Scenario 2	7.63
Scenario 3	4.52

Table 7. Economic evaluation of the principal bioenergy products.

Parameter	Hydrogen (Production Cost/Kg)					Ethanol (Production Cost/Liter)		Electricity (Production Cost /KW)	
	Sc. 1	**Sc. 2**	**Sc. 3**	**Sc. 4**	**Sc. 5**	**Sc. 3**	**Sc. 5**	**Sc. 2**	**Sc. 3**
Raw Materials	0,44	0,61	0,55	17,58	6,21	0,08	0,87	0,0062	0,0073
Operating Labor	0,02	0,02	0,02	0,18	0,06	0,00	0,01	0,0005	0,0007
Utilities	1,03	1,95	1,36	5,79	1,80	0,74	0,68	0,0004	0,0101
Operating Charges, Plant Overhead, Maintenance	0,02	0,02	0,02	0,14	0,05	0,001	0,01	0,0004	0,0005
General and Administrative Cost	0,01	0,04	0,06	1,10	0,30	0,002	0,07	0,0008	0,0018
Depreciation of Capital	0,04	0,04	0,04	0,35	0,14	0,001	0,03	0,0008	0,0012
Total	**1,57**	**2,67**	**2,05**	**25,15**	**8,56**	**0,82**	**1,68**	**0,01**	**0,02**