Evaluation and analysis of the coffee cut stems as raw material for the production of sugars for ABE fermentation

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ABSTRACT

Lignocellulosic biomass is generally considered as a promising feedstock for the production of value added compounds, due to its availability, its low cost and its potential sustainability. Coffee cut-stems (CCS) are a cut of 15-20 cm of length above the land where the coffee plant is cultivated and it is obtained by crop renewal. Its high cellulose content makes it a potential sugar platform for different products. In this sense, the objective of this work is to determine the potential of CCS as a raw material for ABE (acetone-butanol-ethanol) fermentation in technical, economic and environmental terms. The overall ABE fermentation was simulated based on experimental results using the commercial software Aspen Plus to obtain the mass and energy balances. The operating costs were calculated using the software Aspen Economic Analyzer. Aditionally a scale analysis was performed to determine the influence of inflow of raw material on the Net Present Value of the process, the influence of the cost of the raw materials and the production cost of ABE solvents. The obtained yield for the process was 130 kg ABE per ton of CCS. The obtained production costs of each product were above the market price for a base case of 80 ton/h. The process simulated demonstrated a Minimum Processing Scale for Economic Feasibility (MPSEF) of 69 ton/h of CCS. Finally an environmental assessment using the Waste Reduction Algorithm (WAR) software was proposed confirming a medium environmental impact.

Keywords: *Coffee cut stems, ABE fermentation, Net Present Value, Minimum Processing Scale for Economic Feasibility*

1. INTRODUCTION

According to the International Coffee Organization (ICO), annual coffee production has increased from 140 to 152 million bags of 60 kg since 2010 [2]. For this reason, finding an alternative to the byproducts of coffee processing has become a research center. Coffee pulp and husk are generated during coffee processing. There are the first by-products of the industrial process, and account for 29% and 12% of the overall coffee cherry (dry weight). Another by-product is the coffee silver skin, which is produced during the toasting process which represents between 1 and 2% of the total coffee bean. The spent coffe grounds is another byproduct of coffee processing. This is generated during the production of solubilized instantaneous coffee, by means of which roasted and ground coffee beans are treated with value or steam for the production of the coffee extract. It is estimated that 650 tons of coffee produce one ton of spent coffee grounds [1]. A sub-product that is not considered in many studies is coffee cut steams.

The coffee cut steams (CCS) are considered an abundant waste resulting either by cutting or by coffee crop renewal. It is estimated that an average of 17 tons of dry wood per hectare will be generated [3]. This implies a large amount of lignocellulosic waste that can be exploited to increase the country's energy matrix. At present, several studies have been carried out in which obtaining value-added products is sought from CCS. Among these is the gasification of CCS which can be used for the production of bioenergy especially for the production of hydrogen and electricity and biochemical products such as ethanol, due to its high availability [3]. Aristizabal et al evaluated the production of ethanol, octane, nonane, furfural and HMF (furan-based compounds). As a result, the authors obtained that the integration of products under the concept of biorefinery improves costs, making viable a process [4]. In this case the authors concluded that CCS can be an interesting raw material for producing simultaneously energetic vectors.

Currently, the interest in obtaining butanol fermentation is once again taking force, because it is an important chemical with many applications as fuel (the replacement of the fossil raw materials [5]) and fuel additive in the production of solvents, plasticizers, butylamines, amino resins, butyl acetates, detergents, cosmetics and vitamins. These characteristics make it suitable for its implementation in a biorefinery [6] [7]. Half of the butanol production (10–12 billion pounds of butanol annually) is used in the form of butyl acrylate and methacrylate esters, which are employed in latex surface coating, enamels and lacquers [8]. Butanol has several advantages over ethanol as a fuel additive or fuel substitute. It has an energy content that is similar to gasoline, so, less volume is required than ethanol to achieve the same energy output. Finally, this product has a lower vapor pressure compared to ethanol, and is therefore safer during transport and use in car engine [9].

Butanol is currently industrially produced from petroleum or fermentation of corn, cassava or molasses as substrate using several *Clostridium* strains [10]. Three main components, including acetone, butanol and ethanol (ABE) are simultaneously produced from the above mentioned lignocellulosic materials. Additionally, the high availability of lignocellulosic material in a country like Colombia, allows carrying out a study of the use of the coffee cut stems for the production of butanol. The coffee cut stems is a by-product of the coffee harvest, annually it is wasted by the companies that produce it, so its cost would only be associated with transportation. In a typical batch ABE fermentation, only 12-15 g/L butanol and 20-25 g/L total ABE can be obtained through a period of 40-60 h until the fermentation stops due to inhibition [11], generating that the recovery of the solvents is complicated and expensive. For this reason, different product recovery technologies have been developed such as adsorption, pervaporation, perstraction, gas stripping, liquid-liquid extraction and among others [12].

In Colombia, electricity generation is mainly based on hydroelectric power (69.97%). Biomass as an energy source can be an alternative energy resource, which represents 0.57% of the energy generated in the country [3]. The economic viability of a process is determined from the evaluation of variables such as investment costs, costs of raw materials, fixed costs, variable costs, utility costs, among others. From these variables it is possible to calculate the net present value of the process (NPV) in order to analyze the economic balance and determine if the costs of profit are greater than the expenses (NPV greater than 0, makes the process economically viable). If, on the other hand, the economic balance shows that the costs are higher than the gains from the process (negative NPV), the process is economically unfeasible

The aim of this work is to conceptually design the production of biobutanol using process engineering tools and stoichiometric approaches. ABE fermentation was simulated using the commercial software Aspen Plus® to obtain the mass and energy balances. With this information the economic analysis was carried out based on the methodology proposed by Peters et al. [13] for different scales of processes, in order to calculate the Minimum Processing Scale for Economic Feasibility (MPSEF) of biobutanol production using CCS. Then the environmental evaluation of the process was performed using the software WAR GUI (Chemical Process Simulation for Waste Reduction) developed by United States environmental Protection Agency (EPA).

2. METHODOLOGY

2.1 Description of the simulated process

For develop of the process and flowsheet were used process simulation tools. The objective of this procedure was to generate the mass and energy balances from which the requirements for raw materials, consumables, utilities and energy requirements are calculated. The simulation was performed using Aspen Plus software. Non-Random Two-Liquid (NRTL) thermodynamic model was applied to calculate the activity coefficients of the liquid phase and Soave Redlick Kwong was used for description of the vapor phase [14]. The software does not have lignin, hemicellulose, cellulose, biomass and enzymes as compounds of its database. For this the properties of these compounds were taken from the NREL/MP-425-20685 "Development of an ASPEN PLUS Physical Property Database for Biofuels Components" [15].

The characterization of CCS required for the respective calculations is in Table 1. The process consists of three main steps: pretreatment of raw material in order to extract the sugars, ABE fermentation and separation of the product. In this case, the three main products produced during the fermentation (acetone-butanol-ethanol) were taken as products, in order to generate greater added value to the process. However butanol is produced in greater proportion, hence its greater relevance.

Table 1. Composition of the CCS used as substrate for ABE fermentation [16]

Component	**%**
Moisture	4
Cellulose	38.88
Hemicellulose	32.61
Lignin	9.71
Extracts	13.59
Ash	1.21

2.1.1 Pretreatment stage

This stage consists of three main steps: reduction of particle size, hydrolysis with dilute acid and enzymatic saccharification. In detail, the particle size of the dried raw material considered as feed of the overall process is between 10 cm - 16 cm. For this reason a milling step is included in the process for decrease the particle size until approximately 2 mm. The milling process is simulated with two gyratory mills. In first mill the outlet particle diameter is 2 cm and in second mill the outlet particle diameter is 0.5 mm.

After the milling process, the raw material is hydrolyzed with dilute acid. Sulfuric acid at concentrations usually below 4 wt% has been one of the most interest studies developed in recent years, due to that the implementation of this pretreatment is considered inexpensive and effective [17]. Dilute-acid pretreatment removes most of the hemicellulose content in the raw material based on the kinetic expressions reported by Jensen et al., [18]. The product of this process is a dissolved sugars stream which improves the enzymatic accessibility and glucose yields. The conditions chosen are: 121℃, 2 bar, residence time of 15 minutes and solid liquid-ratio 1-10.

Before starting the saccharification step was necessary separate the solid (rich in cellulose) and liquid (rich in pentose) fraction from dilute acid reactor. Then the stream rich in cellulose is carried to the enzymatic hydrolysis. A cellulase enzyme is employed in this stage. According to standard method published by the National Research Energies Laboratory (NREL) the conditions to carry out the enzymatic hydrolysis stage were: 50℃, 1 bar, biomass concentration of 15 g/l and enzyme concentration between 1% and 3% [19]. According to Quintero et al. [20] for CCS the cellulose conversion to glucose is about 92.65%. The main products of this step are rich-hexoses liquor and a solid residue rich in lignin which is separated by filtration.

2.1.2 ABE fermentation

The fermentation step is carried out with *Clostridium acetobutylicum* when glucose is considered as carbon source. Initially the glucose rich liquor produced in the enzymatic hydrolysis was sent to sterilization (121 °C) in order to inactivate any biological activity. Later the fermentation process is carried out based on stoichiometric equations for solvent production from glucose [21] and yields of 20–30 g/L with an acetone-butanol-ethanol ratio of 3:6:1 due to inhibition limits [22], [23]. Afterwards, cell biomass is separated from the culture broth which contains approximately 2-5% (w/w) of ABE. Additionally at this stage, carbon dioxide and hydrogen are produced as by-products, which are separated by a gas purge.

2.1.3 Separation stage

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 [24]. This stage consists of four distillation columns due to the mixture of ABE solvents is highly diluted. The simulation of the columns in all cases required the definition of preliminary specifications using the DSTWU short-cut method included in

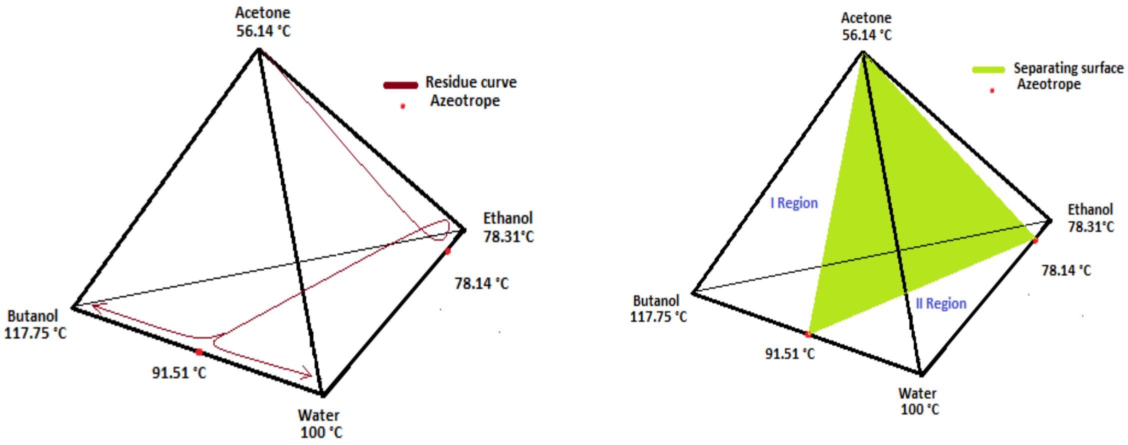
Aspen Plus. This procedure employs the Winn UnderwoodGilliland method that provides an initial estimate of the minimum and actual number of theoretical stages, the minimum and actual reflux ratio, the feed stage, and the distillate to feed ratio. With these results the rigorous calculation of the distillation columns is performed using the RadFrac model of Aspen Plus based on the MESH equations. In order to study the effect of the main operation variables as reflux ratio, number stages, feed stage and distillate to feed ratio on the products composition, a sensitivity analysis in each column was performed.

Aditionally the topological characterization was carried out based on the methodology reported by Pisarenko [25] in order to identify the possibility of separation by distillation of the four components mixture. In this way, a review of the mixture is carried out by determining the temperature of the possible binary and ternary azeotropes at 1 atm of pressure. With this characterization, the residue curves of the regions and the separation regions are determinate. In Table 2 are listed these azeotropic compositions.

Table 2. Composition and temperatures of azeotropes predicted with NRTL-RK model at 1 atm

Mixture	**Molar composition**				**Temperature(°C)**
	B	**A**	**W**	**E**	
W-B	0.5	-	0.5	-	**91.51**
E-B	-	-	0.04	0.96	**78.14**

According with data reported in Table 2, quaternary diagrams of the mixture are showed in Fig. 1.



(a) (b)

Fig.1 a) Residue curves in the tetrahedral (b) Separator surface in the tetrahedral a 1 atm.

As can be observed, the trajectory of the residue curves divides the tetrahedron into 2 separation regions. Depending on the feed composition of the tower, the trajectory separation is determined. Fig. 2 shows the complete flowsheet for the ABE fermentation used in this work. Tower 1 is used to remove about 95% of the water, by distillate a mixture of ABE solvents is obtained with water. This stream enters to the Tower 2 obtaining by distillate an acetone-ethanol mixture and by bottoms an azeotropic butanol-water mixture (50% wt). The first mixture is sent to Tower 3 in order to separate the acetone and ethanol. The second mixture is sent to a liquid-liquid extraction step (decanter) to obtain an organic phase rich in butanol (97% wt). Finally this stream is sent to a dehydration zone which is equipped with molecular sieves to obtain 99.6% wt butanol [26].

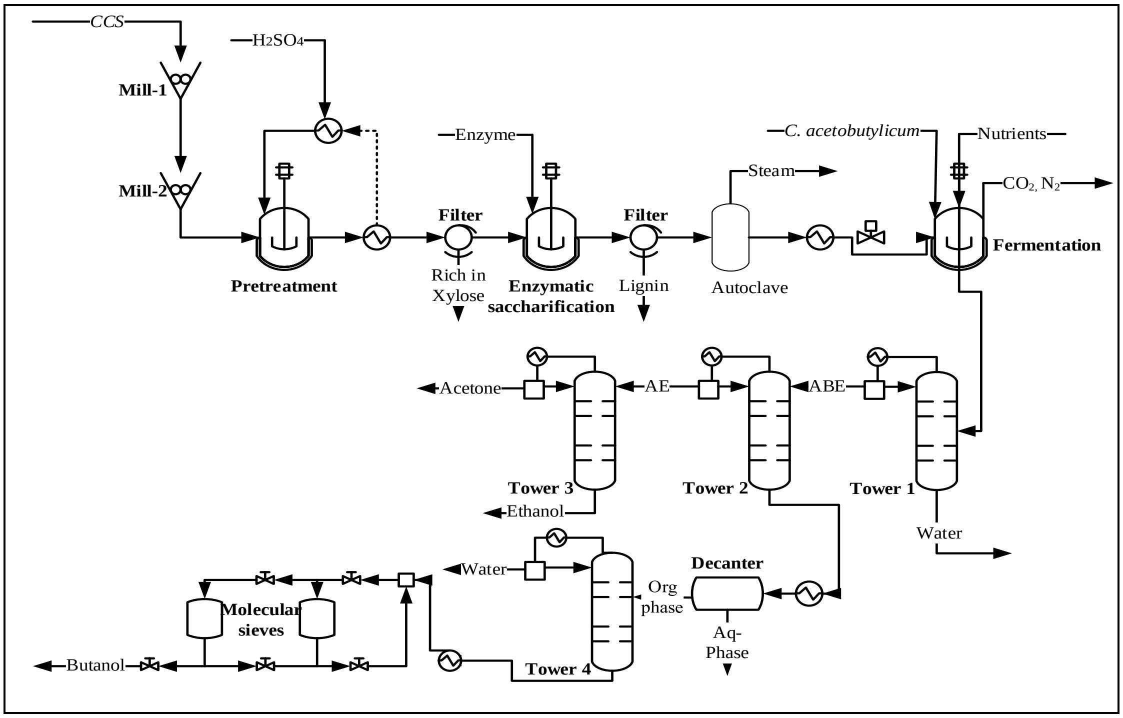


Fig. 2 Process flow diagram of the production of ABE using CCS as substrate

2.2 Economic assessment

In order to evaluate the economic viability of the conventional ABE fermentation, an analysis was carried out that included the different fixed and variable costs of the process. 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. The capital depreciations, maintenance costs, labor costs, fixed charges, general and administrative costs and the plant overhead were calculated based on the economic evaluation methodology for chemical processes of Peters and Timmerhaus [13]. This analysis was estimated in US dollars for a 10-year period at economic typical conditions of Colombia (annual interest rate of 17%, income tax of 25%), considering the straight-line depreciation method. Table 3 presents raw material, utilities and product costs. Economic data used in this analysis correspond to Colombian conditions such as the costs of the raw materials, income tax, utility cost, labor salaries, among others, were incorporated in order to calculate the production costs per kilogram of each product (ABE). This was calculated using an economic allocation factor between the total incomes of each product with respect to the total cost of the process avoiding over-assignment of cost [27].

Table 3. Prices used in the economic evaluation

RAW MATERIALS	COST	Ref
Coffee cut stems	18 USD/ton	[20]
Water	0.33 USD/ m^3	[28]
Sulfuric acid	94 USD/ton	[29]
Enzyme	700 USD/ton	[28]
UTILITIES	**COST**	**Ref**
Electricity	0.1 USD/kWh	[29]
Low pressure steam (LPS)	7.56 USD/ton	
Medium pressure steam (MPS)	8.18 USD/ton	[29]
PERSONAL	**COST**	**Ref**

Operator labor	2.56 USD/h	[4]
Supervisor labor	5.12	[4]
PRODUCTS	**COST**	**Ref**
Butanol	1.43 USD/kg	[30]
Acetone	1.45	[30]
Ethanol	0.45	[30]

With the results Net Present Value (NPV) of the process was calculated, which 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. Then the variations in the market prices of raw materials have an influence on the recovery of investment and generation of profit. For this reason, the market prices of each raw material and product were varied in a range of -100% to 100% and its influence on NPV was evaluated. The results of these calculations will give information about profitability of the process and how much affects these prices to the economic performance. This analysis has a significant importance especially because the ABE solvents are products that has higher variations due his dependence of oil pricing.

CCS is a residue obtained in high amounts (7 million ton/year, Federación Nacional de Cafeteros de Colombia, 2014), which allows proposing a high processing scale; however, ABE solvents has very low production yields. This context makes important to do an analysis of how influences the processing scale of the raw material on the economic performance of the process. In this sense, the influence of the process scale (plant processing capacity) in the production costs and VPN were assessed according to the six-tenths-factor rule [31], in which the capital cost for equipment increases as a function of throughput according. Aditionally, Minimum Processing Scale for Economic Feasibility (MPSEF) was calculated, according to the definition given by Serna-Loaiza [32], which is the processing scale of raw material at which the process will recover the invested amount during the entire lifetime of the project. This means that after the 10-year period of the project, the process will not have earnings or losses. The determination of the MPSEF is very important because it shows the minimum processing scale at which the process will be economically feasible.

2.3 Environmental analysis

The environmental evaluation of the process was performed using the software WAR GUI (Chemical Process Simulation for Waste Reduction) developed by United States environmental Protection Agency (EPA). The method is based on a potential environmental impact (PEI) of the inlet and outlet streams of the process, based on two general areas of interest with four categories in each area: global atmospheric and local toxicological. The PEI is a relative measure of the potential for a chemical or stream waste to have an adverse effect on human health and the environment [33]. The PEI are quantified in human toxicity by ingestion (HTPI), potential for human toxicity by inhalation or dermal exposure (HTPE), potential for aquatic toxicity (ATP), the potential for terrestrial toxicity (TTP), global warming potential (GWP), ozone depletion potential (ODP), acidification or acid rain potential (AP) and photochemical oxidation or smog potential (PCOP) [33]–[35].

3. RESULTS

Initially for the simulation, a base case of 80 ton / h (1920 ton/day) of raw material was taken, which corresponds to 10% of CCS production in Colombia (7 million ton / year). This high process scale was taken to cover a considerable percentage and then perform the scale analysis. After performing the simulation, it was achieved the following production of ABE solvents: butanol 6.08 ton/h, acetone 2.80 ton/h and ethanol 1.52 ton/h. Considering the inflow of CCS, the obtained yield for ABE was 0.13 ton per ton of CCS. After the fermentation, the produced ABE is approximately 13.5 g/h, this means that around of 75% of the produced ABE is being recovered as final product. However, the energy requirements to achieve this percentage are very high (21.50 MJ / kg butanol), value close to that reported by Kurkijärvi et al., with 20.6 MJ/kg butanol[36] and Kraemer et al., with 18.4 MJ/kg butanol [37] . This indicates that the current conditions and the purification stage require high energy requirements to recover considerable amounts of products, compared to other technologies: 13.3 MJ/kg for extraction with oleyl alcohol [37], 13.8 MJ/kg for gas stripping [38] and 8.2 MJ/kg for adsorption–desorption [38].

3.1 Economic assessment

The total cost of the process was 108 million USD for the base case. Fig. 3 presents the contribution of each category to the total costs. It is observed that the category that contributes in greater proportion to the total costs is the utilities due to the high energy demand and cooling of the pretreatment and separation stage. On the other hand, raw materials are the second category that most contributes to the cost with. Of the cost of raw materials, 30% corresponds to cost of CCS, 41% represents the enzyme cellulase added for the enzymatic hydrolysis, 25% corresponds to the sulfuric acid used in dilute acid hydrolysis and 4% for process water.

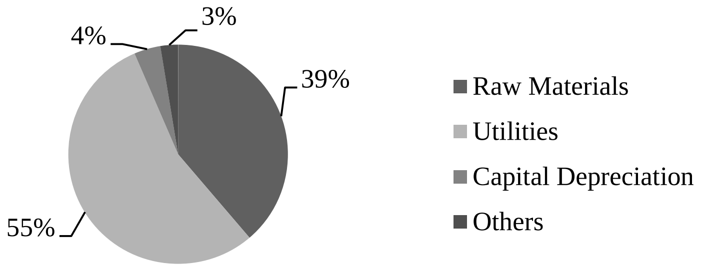


Fig. 3 Cost contribution for the base case (80 ton/h). *Others corresponds to: maintenance (1.14%), labor (0.09%), fixed and general (0.71%) and plant overhead (0.64%)

Table 4 shows the earnings and production cost of the butanol, acetone and ethanol. Due to the butanol flow is higher, this presents the highest allocation factor followed by acetone. Three production costs are lower than the commercial reported sales price, which is an initial indicator of a good economic performance of the process for the base case. In the literature, a production cost value is not easily found. However, Jang et al., [39] report a cost of production of 1.427 USD / kg butanol which is similar to the value calculated in this work. The production cost obtained in this work is slightly high, which can be explained due to the low production yield in the fermentation stage.

Table 4. Earnings from sales and cost production of ABE solvents

Product	Income [mUSD/year]	Allocation Factor (Economic)	Allocated Cost [mUSD/year]	Production Cost USD/kg
Butanol	76.20	0.68	73.90	1.39
Acetone	35.61	0.32	34.53	1.41
Ethanol	6.01	0.05	5.83	0.44

On the order hand, for determine the feasibility of the process de Net Present Value (NPV) was calculated. The NPV is the difference between the present value of the cash inflows and the present value of the cash outflows (including the initial cost) over a period of time. This leads to the cost of the raw material being greater than the cost of the product. Fig. 4 presents the behavior of the VPN of the base case, so in the first 4 years of the project the process is not profitable. This analysis considers a period of 2 years prior to the start of production for the assembly and construction of the plant. For this period of time NPV is negative. This value is attributed to the cost of fixed capital investment which corresponds to 17.96 mUSD. After time 0 the NPV is still negative, which indicates a negative economic balance in which the expenses are higher than the income. Upon reaching 4 years the NPV becomes positive making the process feasible. For a period of 10 years it would be counted with an accumulated cash flow of 19.59 mUSD.

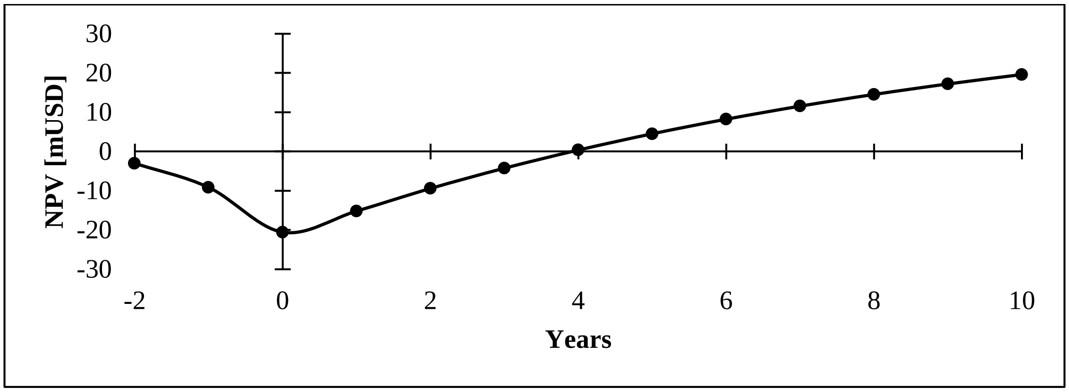


Fig. 4 Net present value of the process over the project lifetime. *Total capital investment.

Fig. 5 shows the impact of the variations in market price of the products and raw material, respect to the recovery of the investment and the generation of profits. For this, the market prices of each raw material were varied in a range of -100% to 100% and its influence on the NPV was evaluated. For raw materials, the price of water does not influence the NVP of the process. However, the price of the enzyme, sulfuric acid and CCS affect the NPV considerably (slope of the line is pronounced). The enzyme is the raw material that most affects the NPV of the process. By increasing the value of your purchase by 50% (700 USD/ton), the NVP of the process becomes negative. Similarly occurs for an increase of more than 50% the price of the raw material (18 USD/ton) and sulfuric acid (94 USD/ton). For the sale price of products, it is possible to observe that the ethanol, although it increases or decreases in price, does not affect the NPV of the process. For the sale price of butanol and acetone, a linear behavior is observed in which an increase in the sales price favors the NVP of the process and a decrease in the sale price disadvantages the NPV of the process. In the case of butanol from a reduction greater than 25% (1.43USD/kg), the NPV of the process is affected in greater proportion. The less impact of acetone and ethanol in NPV is due to the low yields that these products present in anaerobic fermentation.

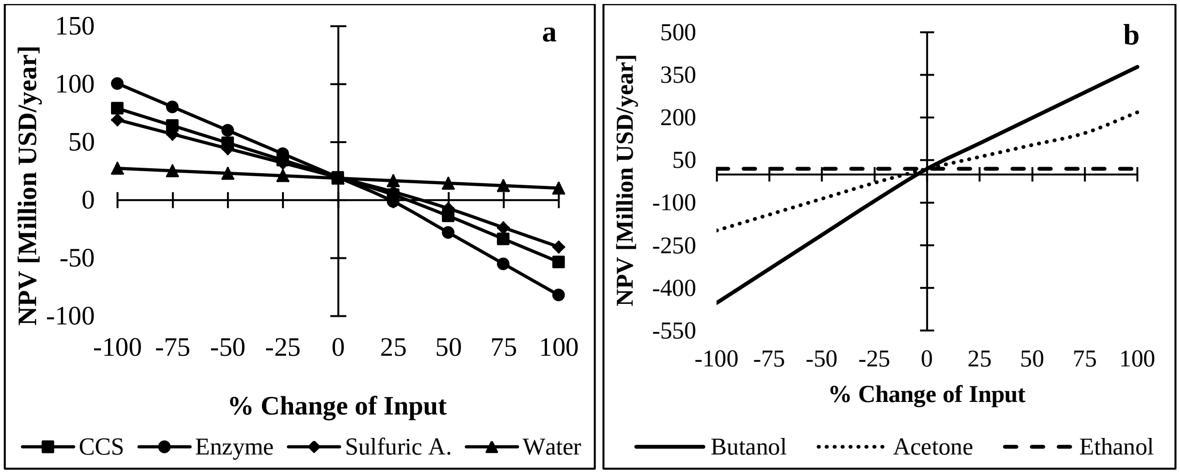


Fig. 5 Influence of the cost of raw materials (a) and the sale price of products (b) in the economic analysis

On the other hand, the scale analysis for the process of production of butanol from CCS is present in Fig 6. The behavior of NPV at different processing scales is analyzed. The analysis is performed for 4 scales of different production. It starts from a 1200 ton / day scale up to 1920 ton / day. For the first two scales analyzed (1200 ton/day and 1440 ton/day) the process is not feasible because the economic balance is higher for production expenses than for income (NVP is not positive). For a production of 1920 ton / day the process is economically feasible. Aditionally it is possible to observe that the MPSEF is 1656 ton/day (69 ton/h), that is, higher values generate profit margins.

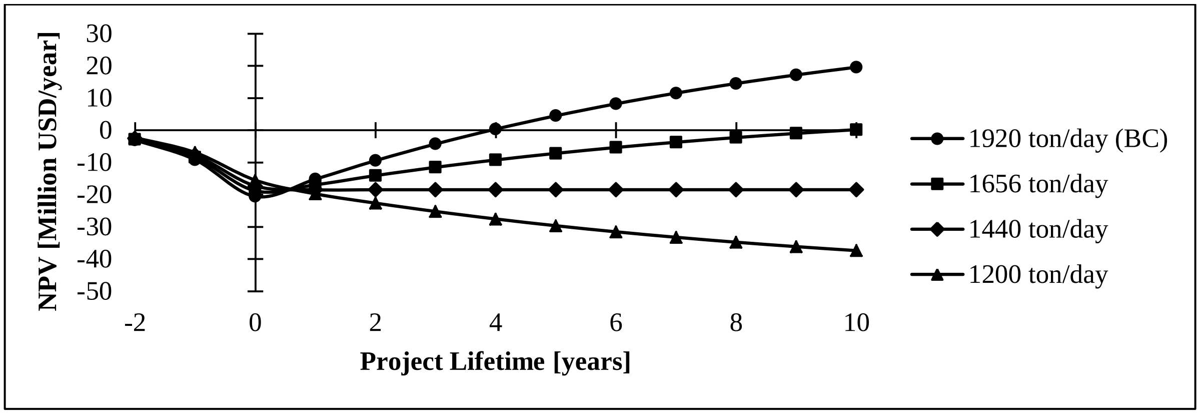


Fig. 6 VPN behavior for different scales of raw material processing

Finally, Fig. 7 shows the analysis of the cost of production of each product depending on the scale of production. The reported sale price for acetone, butanol and ethanol (70% wt) are 1.45 USD / kg, 1.42 USD/kg, 0.45 USD/kg respectively. From the analysis is possible determine that at scales process greater of 1656 ton/day, the production costs of the products is greater at the sales prices on market. Aditionally, It is possible to evidence, low process scales (< 1656 ton per day) generate high productions costs (1.56 USD/kg, 1.58 USD/kg and 0.49 USD/kg, for butanol, acetone and ethanol respectively) and thus, the NPV of the process is negative (see, Fig. 5). Nevertheless, it is noteworthy that processing capacities higher than 1440 ton per day turns the NPV less negative since the production cost is closer to the market price.

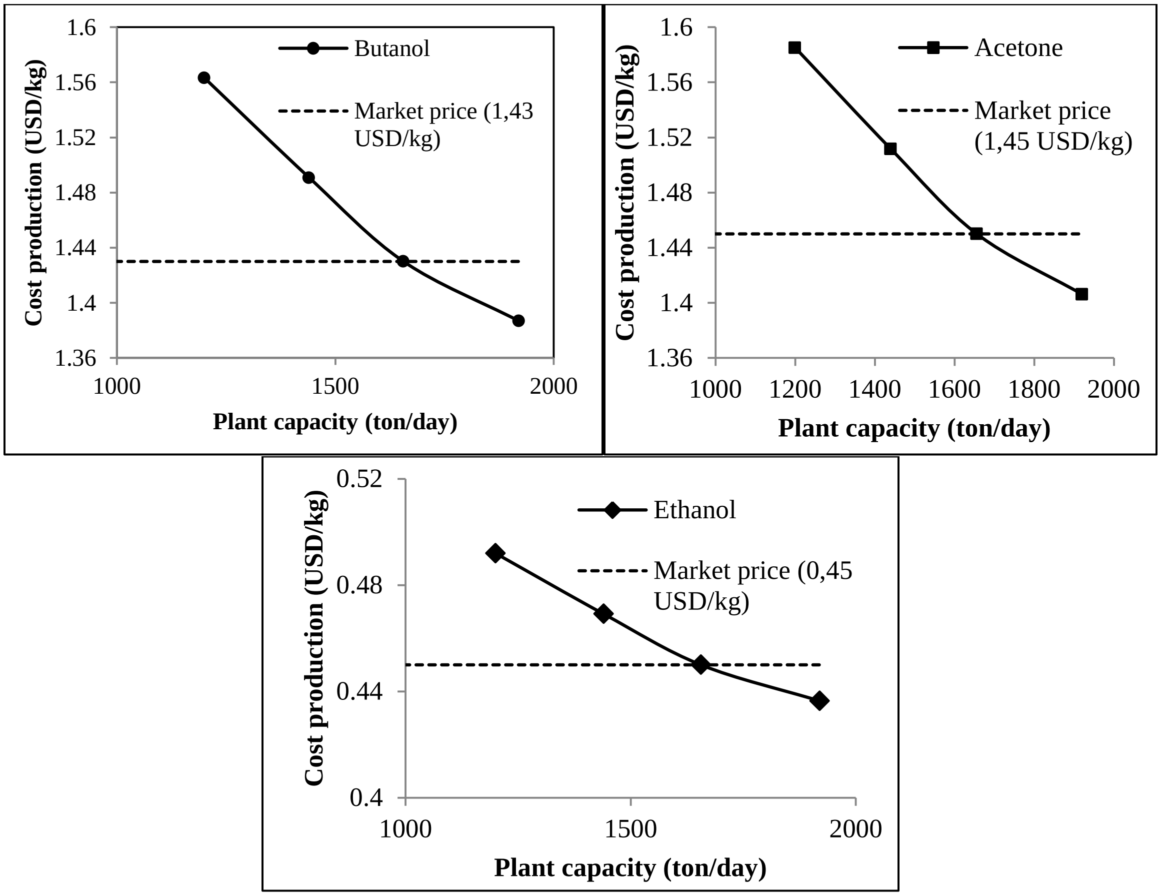


Fig. 7 Effect of the plant capacity in the butanol, acetone and ethanol production cost

3.2 Environmental analysis

Fig. 8 presents the results obtained from the environmental analysis carried out with the software WAR GUI. As a result, it was found that only 3 of the eight categories evaluated generate environmental impact. These are HTPI, TTP and PCOP, related to ingestion toxicity, terrestrial toxicity and photochemical oxidation. The first categories evaluate the impact generated on humans, this means that if the outlet streams are discharged into water, the consumption or contact with these can generate toxicity to people, this is due to the presence of compounds such as solvents and acids in waste streams.

In the case of TTP, the saccharification is one of the processes that generate more pollution when it is poured on the land; due to the stream contains lignin. Finally, the PCOP can be explained due to the solvents that remain in the outlet streams of the stages of purification. These compounds are classified as volatile organic compounds (VOC), and are within the main components together with alkanes, olefins, alkynes, aromatics, aldehydes and hydrocarbons, that intervene in the formation of fog in the presence of NO_X gases and ultraviolet light [38].

The potential environmental impact (PEI) is not only affected by the composition of the waste streams of the process. It is also affected by the energy required for the process and this process demands a lot of energy in the pre-treatment and separation stage.

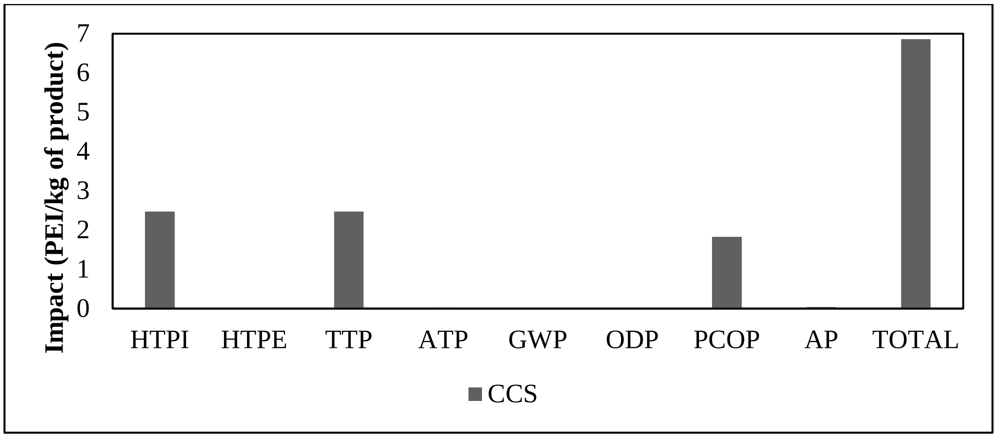


Fig. 8 Potential Environmental Impact (PEI) calculated for ABE production for the base case (80 ton/h)

4. CONCLUSION

This work demonstrates the production of biobutanol through a conventional ABE fermentation with a hydrolysate of lignocellulosic residue (CCS) as carbon source. The purification stage allows obtaining acetone and ethanol as co-product. The fermentation stage, associated to the microorganism still requires increasing the productivity and purification yields through the implementation of nonconventional technologies such as gas stripping, extractive fermentation, adsorption, etc. However, the economic assessment shows a good performance, achieving a payback period of 3.9 years and generating positive income margins for the base case (80 ton/h). The production cost achieved in this work remains within the reported ranges and above of market price. For the other hand the analysis of the scale shows that this process has good economic performances at high-scales, given that the Minimum Processing Scale for Economic Feasibility corresponds to 69 ton/h (1656 ton/day), a value below to 10% of the Colombian production of CCS. Regarding the environmental analysis, it is observed that the waste streams that contain lignin, sugars and solvents generate negative environmental impacts. Therefore, the study should be complemented with an assessment of these streams.

5. ACKNOWLEDGEMENTS

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