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Techno-economic and energetic assessment of hydrogen production through gasification in the Colombian context: Coffee Cut-Stems case

Carlos A. García^a, Jonathan Moncada^b, Valentina Aristizábal^a,
Carlos A. Cardona^{a,*}

^a Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia sede Manizales, Cra. 27 No. 64-60, Manizales, Colombia

^b Energy & Resources, Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, Netherlands

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ABSTRACT

The use of agricultural residues for bioenergy production is gaining importance at a global scenario. There are multiple options to convert these residues into bioenergy carriers such as thermochemical processes (e.g., gasification). In this paper, a techno-economic assessment is carried-out to compare the stand-alone and biorefinery production of hydrogen through gasification as potential scenarios for bioenergy production. Experimental gasification procedures were carried out aiming to determine initial conditions and parameters for the simulation approach. The results demonstrated that the production of hydrogen based on the concept of a biorefinery can improve the profitability of the processes compared to that based on the stand-alone way. Thermochemical processes seem to be a potential technology for bioenergy production in Colombia; however, it also needs to be benchmarked with other technologies in order to provide insights on future development of bioenergy programs in Colombia.

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Introduction

The electric energy matrix in Colombia has been transformed throughout the last years. Currently, the electricity generation in Colombia is distributed as follows: hydropower is the most used technology in the generation of electricity accounting to 69.97%, followed by Gas- and Coal-thermal plants accounting to 9.85% and 8.20%, respectively. Liquid (diesel) and gaseous fuels account to 11.30% of the generated electricity in Colombia. In contrast, the electricity generation from renewable energy sources such as biomass and wind account to

0.57% and 0.11%, respectively [1]. Table 1 presents the installed capacity of electricity generation in Colombia and its distribution among different technologies, respectively.

Biomass plays an important role in the energy matrix of the country as it is today the second largest renewable energy resource after hydropower. The historical demand of biomass in the form of wood, cane bagasse and biomass residues has remained relatively constant since 1975 ranging between 3.72 and 4.47 Mtoe [2]. The use of biomass for energy purposes depends of the type, composition and its application. Wood is used as traditional fuel for cooking and heating in farms,

* Corresponding author.

E-mail address: ccardonaal@unal.edu.co (C.A. Cardona).

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Table 1 – Installed capacity of electricity generation in Colombia.

Technology	Installed capacity (MW)	Share (%)
Hydropower	11,500.5	69.97
Gas–thermal	1619.5	9.85
Coal – thermal	1348.4	8.20
Liquid fuels	1592.0	9.69
Gas – liquid fuels	264.0	1.61
Biomass	93.2	0.57
Wind	18.4	0.11

where its energy density is very low. However, different gasification projects have been implemented in Colombia aiming to produce bioenergy for towns that are not connected to the Interconnected National System (SIN). Gasification is one of the most promising technologies for the production of energy using reciprocating engines.

In coffee-producing countries such as Colombia, coffee tree wood as waste is abundant, either from cuts or renovations, because between 80,000 and 90,000 coffee hectares are renovated per year, from which on average 17 tonnes of dry wood per hectare can be obtained. These residues would serve to produce, approximately, 690 GWe every year [3]. Currently, most of the forest residues are used directly in combustion processes for cooking and heating in rural areas. According to Roa [4], CCS have a higher calorific value (19.75 MJ/kg) than other by-products of the coffee process such as the coffee pulp (15.88 MJ/kg) and coffee dust (17.90 MJ/kg). This residue is normally used in the mechanical drying of the coffee grain with a consumption of 4 kg of CCS to dry 12.5 kg of dry coffee grain [5]. However, the energy content of these residues is not properly used and the direct emissions related to the combustion processes are relative high. For this reason, different thermochemical and biochemical methods have been tested for the transformation of these residues into bioenergy and/or biochemical products. Bioethanol, furfural, octane, nonane, Hydroxymethylfurfural (HMF) and synthesis gas are some of the products that can be obtained from CCS as raw material [6,7].

Different ways to obtain bioenergy from this woody residue have been widely studied. Thermochemical technologies such as pyrolysis, combustion and gasification are the most interesting concepts, focusing on the use of biomass as source for energy at positive net balances [8]. From these processes, biomass gasification has attracted the highest interest as it offers higher efficiencies compared to combustion and pyrolysis [9–11]. The produced synthesis gas from the gasification, as a bioenergy platform, can be used to produce a variety of bioenergy and chemical products, with less environmental emissions [12]. Zainal et al. [13], evaluated the production of electricity from a downdraft gasifier using wood chips as feedstock. As main result, the cold gas efficiency of the gasifier was approximately 80%, whereas the electric overall efficiency was in the order of 10–11%, with a biomass consumption of 2 kg biomass per kWh. Lv et al. [14], studied the production of hydrogen using different gasifying agents (air and a mixture of oxygen/steam) in a downdraft gasifier. From the evaluated gasifying agents, the mixture between oxygen and steam yielded the highest hydrogen content with less

energy consumption. Despite the relative low hydrogen content in the air gasification, the generated synthesis gas can be used in a variety of applications such as electricity generation, ethanol production and hydrogen separation [15].

This paper evaluates the techno-economic assessment of three scenarios for bioenergy production. Stand-alone and biorefinery schemes were considered in the economic analysis of the proposed scenarios. Coffee Cut-Stems (CCS) were characterized in terms of the chemical composition (cellulose, hemicellulose, lignin, extractives and ash), proximal analysis (volatile matter and fixed carbon) and elemental analysis (carbon, hydrogen, oxygen and nitrogen). Experimental procedures were carried out in a pilot scale gasifier using CCS as feedstock and air as gasifying agent in order to evaluate the content of the gaseous species in the generated synthesis gas. Mass and energy balances, obtained from the simulation procedure, were used as starting point in the economic assessment of the proposed scenarios.

Methodology

The physicochemical characterization of Coffee Cut-Stems (CCS) was used as the starting point for the experimental and simulation procedure of the air gasification. A pilot scale (10 kW) gasifier was used for the experimental procedure in the determination of the main gaseous species of the synthesis gas from the CSS gasification. Different computational tools were used to carry out the simulation of the air gasification. The general simulation procedure was carried out using the software Aspen Plus V8.0 (Aspen Technology, Inc., USA). The results from the experimental and simulation procedures of the air gasification using CCS as feedstock were compared in terms of hydrogen, carbon monoxide and carbon dioxide content. Besides, the higher heating value of the synthesis gas was also compared. Three scenarios were proposed: the first scenario involves the stand-alone production of hydrogen and the remaining two scenarios involve the integrated production of electricity and ethanol along with the hydrogen production, respectively. Mass and energy balances from the simulation procedure were used by the software Aspen Process Economic Analyzer (Aspen Technology, Inc., USA) to determine the economic performance of the proposed scenarios. For this purpose, the hydrogen production cost and the Net Present Value (NPV) were used to evaluate the economic profitability of the process schemes. The NPV gives an insight of the amount of money that must be available at present time considering the profit of the project, payoff of the investment, and normal interest on the investment [16].

The optimum size of a processing plant involves tradeoffs between economies of scale with larger plants and increased costs of feedstock transportation [17]. For this reason, the effect of the plant capacity in the hydrogen production cost and the Net Present Value (NPV) was evaluated. Low scale processes have high initial investment and operation costs, in contrast to high scale processes; however, large plant sizes mean larger transportation distances for collecting biomass. Based on this statement, another important parameter that must be considered in the economic assessment involves the cost associated to biomass, which can be divided in two

components: the biomass purchase price and the transportation cost from one region to the plant location. In this paper, the transportation costs were not considered since the biomass logistics from the harvesting region to the processing plant location was not studied. On the other hand, the biomass purchase price was calculated considering the international coffee selling price, the amount of CCS that is obtained from a harvested coffee tree and the economic contribution of the total coffee production cost to the wood tree residue cost.

Raw material location

Colombia is the fourth largest coffee producer in the world after Brazil, Vietnam and Indonesia [18]. Most Colombian coffee growing areas are located in the Andean region, which comprises 8 departments. Caldas (5°06'N 75°33'O) is one of these departments with a great coffee growing nature. Caldas has a cultivated area of 59,757 ha with an annual coffee productivity of 1.05 ton of Coffee per hectare. In this paper, Caldas was selected as the raw material location for the techno-economic assessment of bioenergy production through gasification using CCS as feedstock.

CCS purchase price

The calculation of the CCS purchase price was performed based on three parameters: the international “pergamino” coffee price, the mass ratio between the “pergamino” and cherry coffee production, and the CCS productivity from the cherry coffee. Some of the considered assumptions in the CCS purchase price are summarized below.

- The cherry coffee is the grain that is harvested from the coffee tree and it is used as raw material in the coffee processing process. The “pergamino” coffee is the product obtained at the end of the coffee production process. In order to evaluate the amount of cherry coffee that is required to produce 1 kg of “pergamino” coffee, the National Coffee Research Center (CENICAFÉ) determined the conversion factors between different coffee grain status [19]. Based on the reported data, 4.92 kg of cherry coffee are required to produce 1 kg of “pergamino” coffee.
- According to the National Coffee Federation (FNC), an average of 0.6 kg of CCS are obtained per kilogram of processed cherry coffee [20].
- The international price of the “pergamino” coffee, in the first semester of 2016, in Caldas was 2134.33 USD ton⁻¹ [21].
- It was assumed that the contribution of the “pergamino” coffee price to the CCS price was approximately 5%.

Based on these assumptions, the Coffee Cut-Stems purchase price that was used in calculations had an average value of 23.86 USD ton⁻¹.

Experimental procedure

Coffee Cut-Stems (CCS) used in the experimental procedure were obtained from a farm placed in Chinchiná (4°58'50"N

75°36'27"O) located in Caldas with an average temperature of 21 °C. The raw material was previously dried by exposure to the sun until a moisture content between 10 and 20% was reached. Subsequently, the dried wood residue was chipped using a portable chipper to obtain a particle size between 1 and 2 cm.

Characterization methods

- Chemical composition

The physicochemical characterization of CCS involved the determination of the chemical composition, proximate analysis, elemental analysis and calorific value. The chemical composition of the wood residue was measured in terms of the cellulose, holocellulose, lignin, extractives and ash content based on international standards [22–25].

- Proximate analysis

Proximate analysis is a partitioning of the biomass in three categories: volatile matter (VM), fixed carbon (FC) and ash (ASH). The ash content follows the same procedure before mentioned. The determination of the volatile matter was carried out in a platinum crucible at 950 °C for 7 min according to ASTM D3175 – 11. Fixed carbon was calculated as the difference between the ash and volatile matter content on dry basis.

- Elemental analysis

Elemental analysis includes the identification and quantification of elements in a sample, determination of the elemental composition and trace level elements. The main identified elements in this analysis are the carbon, hydrogen, oxygen and nitrogen or almost always refer to CHON. The quantification of the elemental composition of the raw material was performed in a CHNS elemental microanalyzer with Micro detection system TruSpec (LECO, USA).

- Calorific value

The heat of combustion is the total energy release when a substance, biomass, coal, among others, undergoes complete combustion with oxygen under standard conditions. The determination of the calorific value was based on the American Society for Testing and Materials (ASTM D-5468). The procedure was developed using a calorimeter bomb (IKA Werke model C5003, Brazil) with a measuring cell controller and a refrigeration system. The generated heat during the combustion process was measured using the adiabatic measuring method.

Pilot – scale gasification

The synthesis gas production using air as gasifying agent was performed in a 10 kW gasification equipment (GEK Gasifier 10 kW Power Pallet, California, United States) integrated with a combustion engine and a generator. Fig. 1 presents a schematic process flowsheet of the pilot-scale gasifier used in the

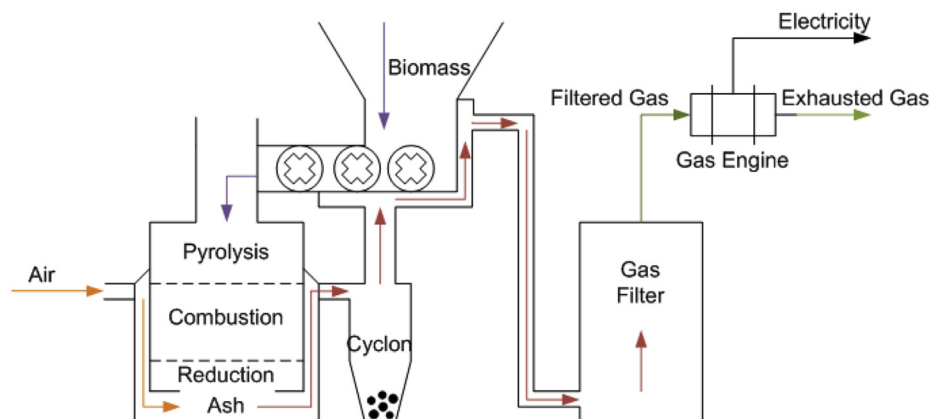


Fig. 1 – Process flowsheet of the pilot-scale gasifier in the 10 kW Power Pallet.

experimental procedure. As mentioned in Section “[Experimental procedure](#)”, the chipped wood residue must have a moisture content between 10 and 20%, since a high moisture content in the raw material causes an increase in the energy requirements of the gasification equipment to evaporate the excess moisture, thus decreasing the energy efficiency [26]. The process starts with the supply of biomass into the hopper. Then, the feedstock passes through an auger and enters into the gasifier reactor. The auger is controlled by a level switch incorporated into the reactor. Then, a torch and gasoline are used to start the reactions. Subsequently, the temperatures inside the gasifier begin to increase, involving different gasification zones: pyrolysis, combustion and reduction. The highest H_2/CO ratio was obtained when the gasifier reaches a temperature above 800 °C. The high temperature synthesis gas was used to heat up the air flow before it enters into the combustion zone. Ash is produced as main by-products from the gasification stages. Ashes are collected through a vibratory grater which separates the ashes from the carbonized biomass (char). Subsequently, the hot syngas passes through a cyclone to separate the remaining ashes and char particles. After the cyclone, the syngas still has enough energy as heat to be used. For this reason, the syngas uses its high heating energy to remove part of the moisture in the biomass that is fed through the auger. The generated gas has some impurities such as tars, water and char particles that must be removed to avoid damage of the gas engine. In this sense, the gas passes through a four-level filter in order to remove these impurities. The first level of the filter contains big pieces of wood (average particle size of 5–10 cm), the second level has smaller pieces of wood (3–5 cm), the third level is filled with shavings from the furniture industry, and the last level consists of a foam filter. In order to ensure the highest H_2/CO ratio, a portable gas analyzer (GASBOARD 3100p, Wuhan, China) is connected at the outlet of the filter and the composition of the syngas, throughout the gasification procedure, is monitored. The gas analyzer measures the outlet gas composition in terms of hydrogen, carbon dioxide, carbon monoxide, methane, oxygen content and additionally, it calculates the calorific value of the syngas. Finally, the purified syngas is submitted to a gas engine which uses it as fuel to generate electricity. The generator has an electrical

capacity between 2 and 10 kW. An overall balance of the process indicates that 1 kg of biomass can produce 0.75 kWh of electricity [27].

Simulation procedure

In order to evaluate the performance of stand-alone and biorefinery ways to produce hydrogen, three scenarios were proposed. One scenario is related to the production of hydrogen in a stand-alone pathway. The remaining two scenarios were evaluated considering the conceptual design of a biorefinery, which is related to three concepts: i) hierarchy, ii) sequence and iii) integration [28]. According to the hierarchy approach, the first step considers the selection of the main products that are going to be targets for the biorefinery design. Hydrogen, electricity and ethanol were selected as main products addressing the hierarchy design to hydrogen, then to ethanol and finally, electricity. Besides, the sequence of the technological routes was established according to the well-known onion diagram, giving importance to the reaction stage [29]. Mass and energy balances were obtained using simulation procedures. The software used for this purpose was the simulation tool Aspen Plus v8.0 (Aspen Technology, Inc, USA). The effect of the hierarchy of products within a biorefinery was used to evaluate the economic performance of the hydrogen production. The main objective of this procedure was to select the scenario, in a biorefinery way, that makes the hydrogen production process more profitable compared to the stand-alone pathway.

Scenarios

Three scenarios for the CCS gasification were proposed to evaluate the effect of the hierarchy decomposition of the products in the economic assessment of the hydrogen production. Stand-alone way (the production of hydrogen as a single product from gasification) was selected as base case for the comparison with the remaining two scenarios, where the conceptual design of a biorefinery was applied. [Table 2](#) presents the description of the three evaluated scenarios considering three products: hydrogen, ethanol and electricity.

Table 2 – Stand-alone and biorefinery scenarios for the hydrogen production.

Technology	Scenario	Products	Description
Gasification	Scenario 1	Hydrogen	100% Raw material for syngas production
	Scenario 2 ^a	Hydrogen + Electricity	50% of syngas intended for power generation and the remaining for the H ₂ production.
	Scenario 3 ^b	Hydrogen + Electricity + Ethanol	70% raw material for syngas production. The remaining 30% for ethanol production.

^a Same distribution of raw material as in the scenario 1.
^b Same distribution of synthesis gas as in the scenario 2.

Scenario 1 considers only the production of hydrogen from the stand-alone process. Two additional scenarios are proposed for the production of hydrogen, ethanol and electricity through biomass gasification. Scenario 2 considers the use of 50% of the generated syngas in the gasification for hydrogen production and the remaining 50% for the electricity generation, using the syngas as fuel in a gas engine. Moreover, scenario 3 considers the ethanol production from a fraction (30%) of the feedstock to the process. The remaining 70% is used in the gasification process for syngas production from which, 50% is used for hydrogen production and the remaining 50% for electricity generation.

Process description

For all proposed scenarios, mass and energy balances were obtained using simulation procedures. The objective of this procedure was to calculate the requirements for raw material, utilities and energy needs. Mathematical modeling of the concentration profiles using kinetic models was performed in software packages such as Matlab (MathWorks, USA).

For the simulation of the biomass gasification, the Grayson-Streed thermodynamic model was used to calculate the activity coefficients of the liquid phase since the model was developed for systems with high H₂ concentration. The Redlich–Kwong equation of state was applied to describe the vapor phase. In the simulation of the ethanol fermentation, the Non Random Two Liquids (NRTL) was used to analyze the behavior of the liquid phase and the Hayden O'Connell equation of state was selected to describe the vapor phase [30]. Additional data such as physical properties were obtained from the work of Wooley and Putsche [31].

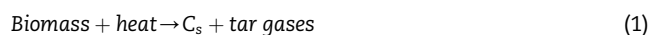
Gasification

The simulation of the air gasification was divided in three stages: pretreatment of the raw material (drying and milling), gasification (enrichment of the syngas) and purification (membranes). The first part of the process involved the pretreatment of the feedstock which consisted on drying the raw material to achieve a moisture content between 10 and 20%. Subsequently, the lignocellulosic residue was chipped to obtain a particle size between 0.5 and 1 cm. These conditions were selected for the simulation according to the requirements of the gasifier from the experimental procedure.

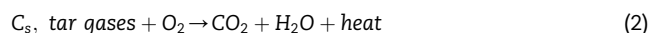
The second stage is related to the chemical pathway of gasification that takes place inside of the reactor as shown in Eqs. (1)–(8). The simulation of the downdraft gasifier was

performed splitting the reactor in three main processes: pyrolysis, combustion and reduction. Dried biomass undergoes into the devolatilization (pyrolysis), where the raw material was decomposed into carbon, hydrogen, oxygen and ash according to the elemental analysis from the experimental procedure. Then, all the components from pyrolysis zone goes into the combustion chamber, where they react with oxygen to produce CO₂, CO, H₂O and heat. The produced char in the pyrolysis and the combustion zone pass to the reduction zone, where char gasification takes place to produce CO₂, CO, H₂ and CH₄. Ash and the remaining char are separated from the syngas using a cyclone.

Pyrolysis



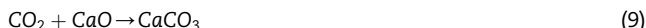
Combustion



Reduction



In order to improve the hydrogen content in the generated gas, an adsorption process was proposed. Carbonation reaction is based on the conversion of carbon dioxide (CO₂) into calcium carbonate (CaCO₃) using calcium oxide (CaO) as adsorbent. For this purpose, the kinetic analysis for the capture and desorption of CO₂ proposed by Nikulshina et al. [32], was used. The presence of CaO in the biomass gasification can increase the hydrogen and carbon monoxide content, and further reduces the tar content in the syngas. For this reason, a coupled two bed reactors, using CaO as adsorbent, were chosen to improve the selectivity of the hydrogen in the synthesis gas. In the first reactor, the carbonation reaction takes place (Eq. (9)) and the CO₂ desorption using air is performed in the second reactor (Eq. (10)).



Finally, a further purification stage is required using hollow fiber membranes, which are widely used in many gas separation industries [33]. Ideal selectivity, separation factor and H_2 recovery were obtained from data reported in literature [33,34]. Choi et al. [34], evaluated the performance of hollow fiber membranes in the separation of H_2/N_2 and H_2/CO mixtures for hydrogen production, and consequently their application in the separation of gaseous mixtures in thermochemical methods such as Steam Methane Reforming (SMR) from which hydrogen concentration up to 30% can be obtained. First, the permeance of the membrane with pure gases (H_2 , N_2 , CO , CO_2) was tested. Then, based on the selectivity of the membrane for the pure components, two mixtures (H_2/N_2 and H_2/CO) were selected to evaluate the hydrogen recovery in these systems. The operational conditions of the membrane were: 50 °C, feed/retentate pressure up to 6 bar and permeate pressure 1 bar. Based on the reported data, 85% molar of hydrogen recovery and 72% molar of hydrogen purity were obtained in the experimental procedures [34]. Therefore, these data were used in the simulation procedure of the hydrogen purification using hollow fiber membranes. Previous treatment of the hydrogen rich gas is required to reach the suitable pressure conditions inside the membrane to enhance the mass transfer of the hydrogen. Maus et al. [35], examined the problems involved in refueling vehicles with compressed hydrogen. According to Maus et al., the filling pressure that must be supplied from the hydrogen storage location should be at levels between 35 and 70 MPa, in order to achieve an adequate volumetric storage density. For this reason, due to the loss of energy after the membrane separation, the hydrogen stream must be compressed to reach the required conditions for the filling station. The process scheme used in the production of hydrogen through biomass gasification is presented in Fig. 2.

Electricity generation

The generated synthesis gas from the biomass gasification has a high energy content, which can be used directly as fuel in a gas engine to produce electricity due to its high H_2/CO ratio. An internal combustion engine burns the gaseous fuel to produce electricity by means of a generator. Normally, the efficiency of these devices is between 27 and 38% and they can provide energy in form of electricity from 30 kWh to 60 MWh [36]. The simulation of the electricity generation from the synthesis gas was based on the syngas mass flow, lower heating value (LHV) of the gas and the efficiency of the internal combustion engine. As a result, the amount of available energy that can be obtained from the synthesis gas was calculated.

Ethanol fermentation

CCS have high cellulose and hemicellulose content, from which fermentable sugars for bioenergy production can be obtained. Due to high cellulose crystallinity and low biodegradability, lignocellulosic biomass may require a

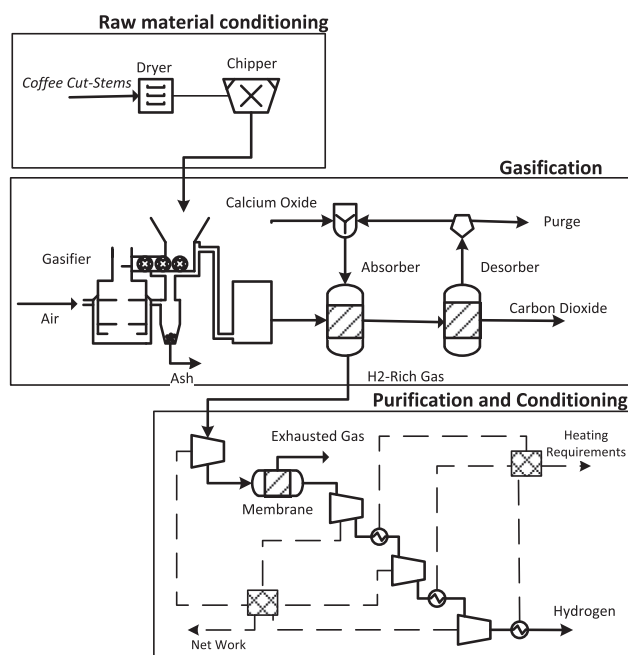


Fig. 2 – Flowsheet of the biomass gasification to produce hydrogen from wood residues.

pretreatment prior to fermentation processes [37]. For this reason, a mild-acid pretreatment and enzymatic hydrolysis were proposed as methods for raw material pretreatment. Acid hydrolysis with sulfuric acid (2% w/w) at 130 °C and solid to liquid ratio of 1:10 were used as conditions in the simulation procedure. Hydrolysis yields were calculated based on the kinetic expression reported by Rafiqul et al. [38], considering the operational conditions mentioned before. One problem associated with the dilute-acid hydrolysis is the formation of toxic compounds such as acids, furfural and phenolic compounds. Alkaline treatment with $\text{Ca}(\text{OH})_2$ is widely used in the hydrolysates detoxification [39]. The simulation procedure of the alkaline treatment consisted in the degradation of furan compounds and consequently, the formation of gypsum that was separated from the hydrolysate by filtration. The chemical pathway of the overliming was obtained from Purwadi et al., [40]. The unconverted fraction of cellulose from the acid hydrolysis can be used to produce glucose by enzymatic saccharification. Enzymatic hydrolysis of woody residues was simulated based on the kinetic expressions reported by Zheng et al., [41], Khodaverdi et al., [42], Kadam et al., [43]. This model correlates the degradation of cellulose and cellobiose with the formation of glucose considering the enzyme charge (cellulase and β -glucosidase). The concentration profiles of the enzymatic saccharification were calculated in the software MATLAB (MathWorks, USA).

The fermentable sugars obtained from the pretreatment stage were converted into ethanol using the bacteria *Zymomonas mobilis* at 30 °C for 30 h. This bacteria has the ability to degrade hexoses and pentoses, as carbon source. Leksawasdi et al. [44], developed a two-substrate model for the fermentation of glucose and xylose by the recombinant *Z. mobilis*. Concentration profiles of ethanol and fermentable sugars

were calculated based on the Leksawadi model in the software MATLAB (MathWorks, USA). Then, the fermentation broth with an ethanol concentration of 5–6% by weight is sent to a downstream process, which consists of two distillation columns and molecular sieves. In the first column, the ethanol is concentrated up to 60%. Then, the ethanol is concentrated until the azeotropic point (96 %wt). Finally, a dehydration stage is required in order to obtain ethanol at 99.6 %wt using molecular sieves [6]. The process scheme of the ethanol production using woody residues is presented in Fig. 3.

Techno-economic assessment

A basic equipment mapping adapted to the economic conditions (tax rate, interest of return, operator and supervisor wages, among others) in Colombia was performed to determine the operating costs of the proposed scenarios including the raw material, utilities, labor and maintenance, general plant and administrative costs. Additionally, the depreciation of the equipment was evaluated considering a project life of 10 years. The mass and energy balances from the simulation procedure were used as a starting point for the economic assessment using the software Aspen Process Economic Analyzer v8.0 (Aspen Technology, Inc, USA). Raw material and utilities costs are the parameters that have the greatest influence in the production costs. Biomass cost was evaluated as mentioned before in Section “Raw material location”. The utilities costs are linked to the heating and cooling requirements of the process, which are obtained from the energy balance in the software Aspen Energy Analyzer (Aspen Technology, Inc., USA).

The economic profitability of the proposed scenarios was evaluated considering the Net Present Value (NPV). This parameter indicates the profits/gains of the process during the project life, which in this case was considered in 10 years. Besides, the production cost of hydrogen and further by-products (electricity and ethanol) were determined, and the influence of the process scale (plant capacity) in the production costs was assessed. Additionally, the effect of the fluctuations in the market price of the main products and reagents, in the economic profitability of the proposed scenarios was evaluated. The main data used in the economic assessment of the proposed scenarios is presented in Table 3.

Table 3 – Utilities, reagents and products market prices.

Component	Price	Units
Sulfuric acid	0.094 ^a	USD/kg
Sodium hydroxide	0.35 ^a	USD/kg
Calcium hydroxide	0.05 ^a	USD/kg
Calcium oxide	0.062 ^a	USD/kg
Fuel ethanol	0.68 ^c	USD/L
Hydrogen	4.47 ^b	USD/kg
Water	1.252 ^d	USD/m ³
Electricity	0.06 ^d	USD/kWh
Propane (Refrigerant)	2.94 ^a	USD/kg
High P. Steam (105 bar)	9.86 ^d	USD/ton
Mid P. Steam (30 bar)	8.18 ^d	USD/ton
Low P. Steam (3 bar)	1.57 ^d	USD/ton

^a Prices based on Alibaba International Prices [45].

^b Based on hydrogen price projections [46].

^c Ethanol price based on statistics of the Biofuels National Federation [47].

^d Prices adapted to the Colombian context [7,29].

Energy analysis

The net energy balance is a sustainability parameter that represents the relation between the produced and required bioenergy in the evaluated scenarios, based on the amount of energy that can supply the bioenergy products in order to mitigate the energy requirements of the processes. The net energy balance (E_n) of the process involves two components: first, the energy content of the bioenergy products in each scenario (i.e. hydrogen (E_{H_2}), ethanol (E_{EtOH}) and electricity (E_w), among others) and the energy needs of the process (i.e. heating requirements ($E_{heating}$), power supply (E_{power}), among others). Positive values indicate that the process is energetically sustainable, since the energy content of the products can fulfill the energy requirements of the process. Negative values means that the energy requirements are higher than the produced energy and thus, the process is energetically deficient.

$$E_n = \sum E_{outputs} - \sum E_{inputs} \quad (11)$$

Considering the main bioenergy products from the evaluated scenarios and their respective energy requirements, Eq. (11) can be expressed as

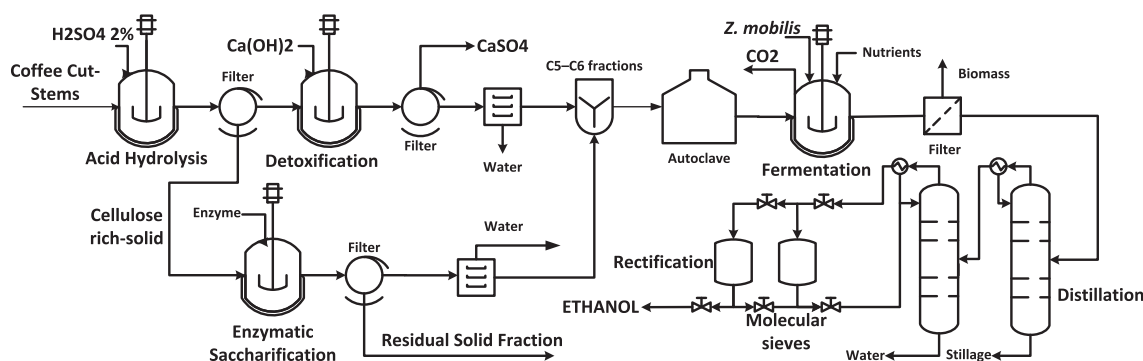


Fig. 3 – Flowsheet of the ethanol production from wood residues using *Z. mobilis*.

$$E_n = E_{H_2} + E_{EtOH} + E_w - E_{heating} - E_{power} \quad (12)$$

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

$$E_{product} = \dot{m}_{product} * LHV_{product} \quad (13)$$

where $\dot{m}_{product}$ is the mass flow of the product in kg/h and $LHV_{product}$ is the heating value of the product in MJ/kg. The amount of produced energy from the synthesis gas, which is used as fuel in a gas engine, can be calculated considering the engine efficiency (η), the syngas flux \dot{m}_{syngas} and the heating value of the syngas. The heating value of the syngas is the sum of the heating value of the gaseous species by the mass fraction of the specie. The equation that describes the electricity generation from the synthesis gas is shown below.

$$E_w = \dot{m}_{syngas} * LHV_{syngas} * \eta_{engine} \quad (14)$$

The heating requirements ($E_{heating}$) were taken from the pinch evaluation of the process using the educational software Hint, which uses the pinch methodology to calculate the exchanger network of a process [48]. The software Hint calculates the energy requirements of the process in terms of the heating and cooling utilities. In the other hand, the amount of power (E_{power}) required in the process was calculated from the energy balance in the simulation procedure.

Additionally, the energy performance of the scenarios were evaluated based on two criteria. First, the energy efficiency of the process considering as only product the hydrogen (Eq. (15)) and secondly, the energy efficiency taking into account all the bioenergy products along with the energy requirements (E_n) (Eq. (16)).

$$\eta = \frac{E_{H_2}}{\dot{m}_{biomass} * LHV_{biomass}} \quad (15)$$

$$\eta = \frac{E_n}{\dot{m}_{biomass} * LHV_{biomass}} \quad (16)$$

where $\dot{m}_{biomass}$ is the mass flow of biomass (kg/h) and $LHV_{biomass}$ is the heat of combustion of the raw material (MJ/kg).

The lower heating value of the raw material can be calculated from the higher heating value (HHV) of biomass fuels on dry basis as shown in Eq. (17).

$$LHV = HHV - h_{fg} \left(\frac{F_{water}}{F_{feedstock}} \right) \quad (17)$$

where h_{fg} is the enthalpy of vaporization of water (approx. 2.26 MJ/kg) [49]. The ratio ($F_{water}/F_{feedstock}$) is the relation between the moisture content of biomass and the amount of feedstock.

Results

Physicochemical characterization of Coffee Cut-Stems

The results from the physicochemical characterization of CCS are presented in Table 4. The high holocellulose content

(cellulose + hemicellulose) of the raw material suggests the potential use of this residue for the production of different platforms such as fermentable sugars that can be used to produce bioenergy and biochemical products. However, due to its high lignin content, this residue requires a prior pretreatment stage in order to increase the biodegradability of lignocellulosic material. A high ash content makes the wood material less desirable as fuel, because a considerable part of the volume cannot be converted into energy [50]. However, the ash content of the raw material is approximately 2%, which do not affect significantly its energy content.

The proximate and elemental analysis is widely used to describe the behavior of the gaseous, liquid and solid components that are obtained through thermochemical methods. The high volatile matter content of the CCS evidences its high potential to produce bioenergy through the direct conversion of the raw material. Char and ash are the main solid residues obtained from a thermochemical process, which constitute the fixed carbon and ash fractions in the proximate analysis; therefore, low content of char and ash are desirable since greater proportion of wood is converted in gaseous species and thus, bioenergy. The calorific value of CCS is related to its chemical composition and varies between 17 and 20 MJ/kg for oven-dried wood [50]. Major elements contributing to the calorific value are carbon, hydrogen, nitrogen, oxygen and sulfur. Elemental analysis can be used to describe biomass fuels, their calorific values [51] and their expected impact on the environment.

Pilot-scale gasification

Fig. 4 presents the results from the CCS gasification for three experimental runs: CCS-1, CCS-2 and CCS-3. It can be evidence that the concentration profiles of the three experimental runs (CCS-1, CCS-2 and CCS-3) changed throughout the gasification time, especially in the amount of generated hydrogen, carbon monoxide and carbon dioxide. An average gasification temperature (850 °C) was kept constant in all the experimental procedures. However, the gasification time varied in each experimental run: CCS-1 was monitored for 90.5 min, CCS-2 for 104.9 min whereas CCS-3 for 64.6 min. The portable gas

Table 4 – Physicochemical characterization of Coffee Cut-Stems.

Moisture Content (%wt)	8.7
Chemical composition (%wt dry)	
Cellulose	40.39
Hemicellulose	34.01
Lignin	10.13
Extractives	14.18
Ash	1.27
Proximate analysis (%wt dry)	
Volatile matter	82.15
Fixed carbon	16.78
Ash	1.07
Elemental analysis (%wt dry)	
Carbon	48.35
Hydrogen	5.93
Oxygen	44.21
HHV (MJ/kg)	19.32

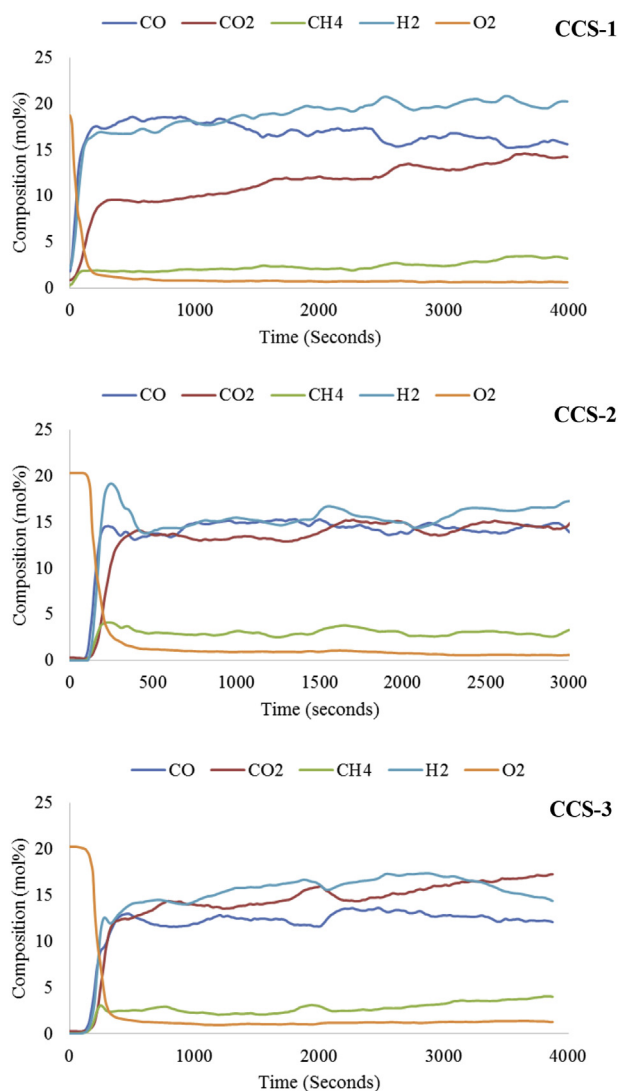


Fig. 4 – Concentration profiles of the different gaseous species obtained from the pilot-scale gasification of CCS.

analyzer is able to detect the composition of the synthesis gas every 5 s, store it and then, plot the composition of the synthesis gas vs the gasification time (see, Fig. 4). The difference between the gasification times from one run to the other is related to the conversion of the wood materials to the synthesis gas (see, Table 5). The highest CCS conversion to syngas (88.2%) was obtained in the experimental run CCS-2, from which an average hydrogen, carbon monoxide and methane concentration of 15.6, 14.4 and 3.1% was determined, respectively. However, the highest hydrogen (18.9%) and carbon monoxide (16.9%) concentration were generated from the

experimental run CCS-1, which had a lower CCS conversion (70.8%). The experimental run CCS-3 had the lowest biomass conversion to syngas, which it was evidenced in the high amount of remaining char and ash from the gasification procedure accounting for the 34.7% of the total CCS fed to the gasifier.

The most important fuel species in the syngas are hydrogen, carbon monoxide and methane. High concentration of hydrogen and carbon monoxide were obtained from the downdraft gasification of CCS using air as gasifying agent as presented in Table 6. The hydrogen content varies from 15 to 20% and the carbon monoxide from 11 to 18%. According to this, the generated syngas has a great energy potential to be used as fuel in a gas engine for the electricity generation because of the high H_2/CO ratio. Despite that the methane content is relative low (2–4%), it can contribute to the relative high calorific value of the synthesis gas as can be observe in Table 6. Moreover, the yield of syngas is in good agreement to other literature reports. Lv et al. [52], evaluated the production of hydrogen-rich gas using air and oxygen/steam as gasifying agents in a downdraft gasifier. As a result, the synthesis gas yield between 0.88 and 0.91 Nm^3 kg biomass was obtained using air as gasifying agent and pine wood as feedstock.

Stand-alone and biorefinery pathways for hydrogen production

Overall performance of the evaluated scenarios

Among the gasification scenarios, the scenario 1 has the highest hydrogen production yield because of the direct use of the generated synthesis gas to produce hydrogen (see, Table 7). Despite the low productivity of the other two gasification scenarios, high yields (>0.012 ton H_2 ton $^{-1}$ CCS) are obtained in comparison to the conversion of lignocellulosic biomass through biochemical methods such as dark fermentation (0.004 ton H_2 ton $^{-1}$ wood) [53]. Electricity is generated as by-product in the scenarios 2 and 3 taking advantage of the high energy content of the synthesis gas. The highest electricity generation is evidenced in the scenario 2 due to the use of 50% of the generated syngas in the CCS gasification in the electricity generation, which can be used to supply the internal energy demand of the process and the surplus can be sold to the national grid. Bioethanol was evaluated as one of the by-products from the biorefinery scheme due to the high lignocellulosic content in the CCS. Scenario 3 involves the production of ethanol along with hydrogen and electricity. Despite the low electricity yield, it was enough to supply the energy requirements of the biorefinery scheme, especially when considering the ethanol separation and purification,

Table 5 – Global mass balance of the experimental gasification runs using CCS as raw material.

Experimental Run	Conversion to syngas
CCS-1	70.8%
CCS-2	88.2%
CCS-3	65.5%

Table 6 – Composition and calorific value of the generated syngas from CCS.

Syngas Components	Composition (%mol)
Hydrogen	15–20%
Carbon monoxide	11–18%
Methane	2–4%
Calorific value (MJ/kg)	4–5.3
Gas flux (Nm^3/h)	6.77–10.37
Gas yield (Nm^3/kg wood)	1.62–0.94

Table 7 – Productivity and yields of the CCS scenarios.

Scenarios	Productivity ^a		Yields ^a	
	Value	Units	Value	Units
Scenario 1	2.1	Ton H ₂ /day	0.042	Ton H ₂ /ton CCS
Scenario 2	0.72	Ton H ₂ /day	0.014	Ton H ₂ /ton CCS
Scenario 3	2.94	MW	5021.7	MJ/ton CCS
	0.68	Ton H ₂ /day	0.012	Ton H ₂ /ton CCS
	10,244.1	Liters ethanol/day	202.2	Liters Ethanol/ton CCS
	1.2	MW	2041.8	MJ/ton CCS

^a Calculated based on 50.7 Ton CCS/day.

which are high energy consumption processes. High bio-ethanol yields (202.2 L ethanol ton⁻¹ CCS) were calculated in the scenario 3. It is noteworthy that the bioethanol yield is higher than other reported yields for different lignocellulosic biomass such as sugarcane bagasse [29], olive stone [54], among others. Additional to the results presented in Table 7, an overall mass balance of the main process streams in each scenario is described in Figs. 5–7. These flow-sheet diagrams were developed based on the data obtained in the software Aspen Plus v8.0 (Aspen Technology, USA).

Techno-economic assessment

Fig. 8 presents the effect of the plant capacity in the hydrogen production cost of the three gasification scenarios. From the sensibility analysis, it is noteworthy that the hydrogen production cost in the scenario 1, at low process scale (<20 ton day⁻¹), is higher than the scenario 2. However, at high plant capacity (>30 ton day⁻¹), the production cost is lower than in scenario 2. Scenario 2 involves the production of electricity and hydrogen, where 50% of the synthesis gas is used to produce electricity, which has a lower added-value in comparison to hydrogen. This behavior evidences that the production of other energetic products, that have a low added-value, does not improve the economic performance of the process when the feedstock is distributed among different processes (see, Fig. 9). However, this behavior was not evidenced in the scenario 3, which produces hydrogen, ethanol and electricity. The contribution of the ethanol to the

economic performance of the scenario 3 is limited by the production cost and volume. High volume and low production costs are required in order to implement the ethanol as a byproduct of the biorefinery scheme. In this sense, the high productivity of ethanol (10,244 L day⁻¹) and low production cost (0.265 USD L⁻¹) improve the profitability of the scenario 3, which has direct influence in the hydrogen production cost since the ethanol represents the highest contribution to the total sales of the products in the biorefinery. Moreover, the generated electricity from the synthesis gas, in the scenario 3, is used to supply the internal energy requirements of the process and the surplus is sold to the national grid with a generation cost of 0.022 USD per kWh. From the scenario 3, a hydrogen production cost of 1713 USD ton⁻¹ was calculated, considering a plant capacity of 50 ton day⁻¹. Higher plant capacities were not evaluated because of the seasonal availability of lignocellulosic biomass and transportation logistic issues.

Based on the results from the hydrogen production cost in each scenario, the NPV was calculated considering a hydrogen market price of 4400 USD ton⁻¹ [46]. Fig. 9 presents the effect of the plant capacity in the NPV of the three gasification scenarios. Scenario 3 seems to be the most promising process scheme for the integral production of hydrogen through gasification under a biorefinery concept, with the highest economic profitability of the three evaluated scenarios. However, the behavior of the NPV in the scenario 1 has a similar trend as the scenario 3, which it is related to the its

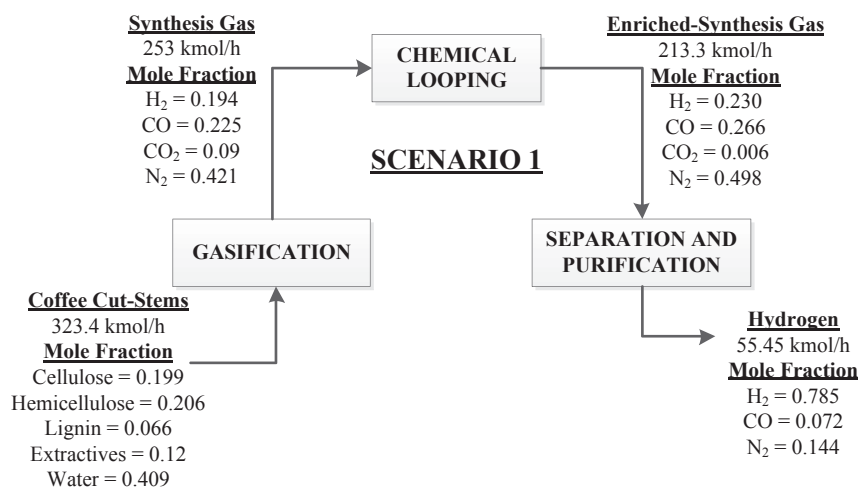


Fig. 5 – Overall mass balance of the scenario 1 for hydrogen production.

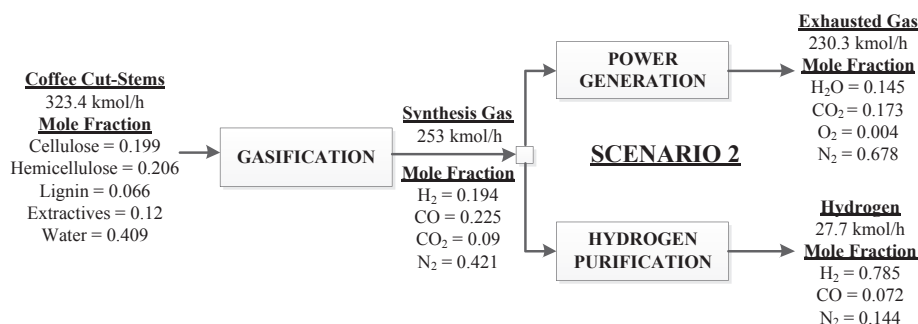


Fig. 6 – Overall mass balance of the scenario 2 for hydrogen and electricity production.

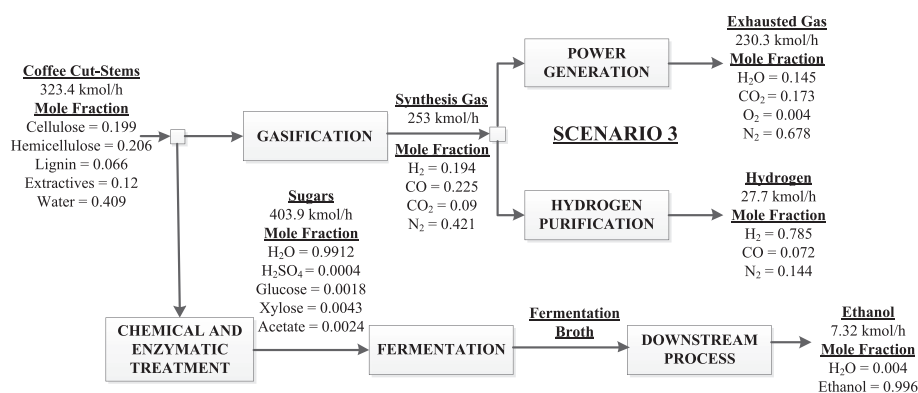


Fig. 7 – Overall mass balance of the scenario 3 for hydrogen, electricity and ethanol production.

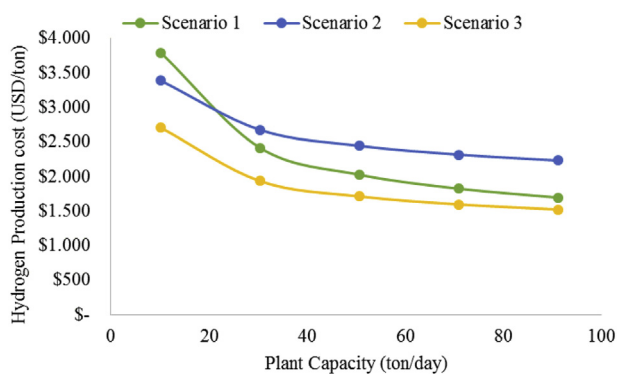


Fig. 8 – Effect of the plant capacity in the hydrogen production cost of the gasification scenarios.

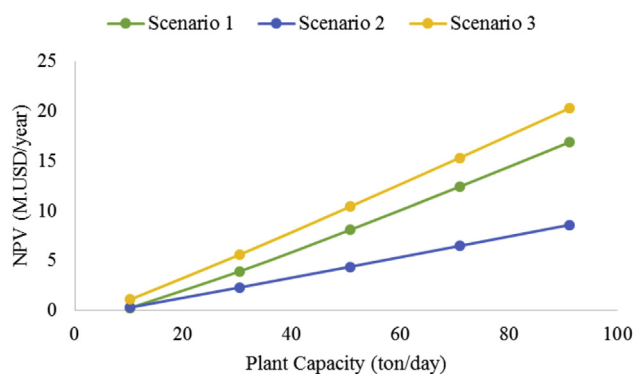


Fig. 9 – Effect of the plant capacity in the economic profitability of the gasification scenarios.

high hydrogen productivity and thus, the profits from this scenario are relative high since hydrogen is the most valuable product (4400 USD ton⁻¹) of the proposed scenarios. Scenario 2 has the lowest NPV due to the production of low added-value products such as electricity. The behavior of the NPV of the three evaluated scenarios can be better evidenced in Fig. 10, where the economic performance of the scenarios was evaluated throughout the project life. In this figure, it can also be noted the time required to recover the initial investment of the process and to start providing positive profits. Scenarios 1 and 2 have the lowest return periods; however, there is a break point where the NPV of the scenario 3 increases in higher proportion than scenario 1. This behavior can be explained

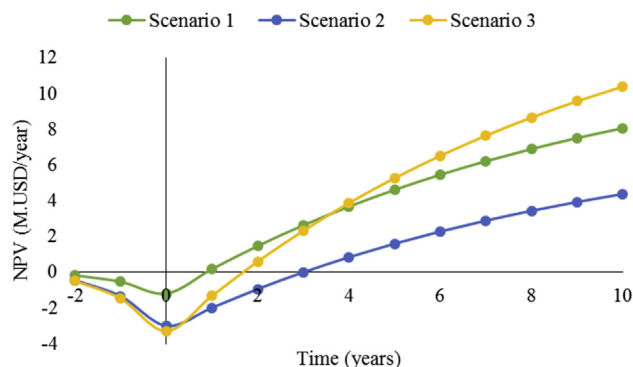


Fig. 10 – Behavior of the NPV throughout the project life.

due to the low-cost ethanol production in the scenario 3 that improves the economic profitability of the process.

The effect of the market price variations for CCS and the main products of the three proposed scenarios (hydrogen, ethanol and electricity) in the NPV of the biorefinery were evaluated considering a plant capacity of 50 ton day⁻¹. Figs. 11–13 present the behavior of the NPV in the three proposed scenarios, respectively. The parameters that have a strong influence in the NPV are the ethanol and hydrogen prices since a reduction of 50% and 90% in the market price, respectively, may turn the process non-profitable. The integrated biorefinery would give negative NPV values if the ethanol and hydrogen reach a selling price below 0.34 USD L⁻¹ and 1100 USD ton⁻¹, respectively. However, according to the National Biofuels Federation (Fedebiocombustibles), this behavior is unlikely since the ethanol market price in the last 6 years has been between 0.54 and 0.78 USD L⁻¹. In the hydrogen case, the scenario is almost the same, since the hydrogen market price will vary between 4400 and 9400 USD ton⁻¹, based on hydrogen production costs projections [46]. CCS and electricity market price do not affect considerably the economic performance of the biorefinery. In the scenario 1 (see, Fig. 11) the hydrogen market price has the strongest influence in the NPV behavior since is the only product obtained from the stand – alone scheme. The same behavior was evidenced in the scenario 2 (see, Fig. 12), despite the fact that electricity is also produced. In contrast, in scenario 3 (see, Fig. 13), the ethanol market price has the strongest influence in the NPV behavior because of the high production volume and thus, its high contribution to the economic allocation of the scenario.

The total production cost of a process scheme was calculated based on different parameters that influenced, positive or negative, the economic performance of the process. Raw material, utilities, capital depreciation and maintenance costs are the most important parameters that have the highest contribution to the total production cost as evidenced in Fig. 14. Scenario 3 has the highest raw material costs since it involves the ethanol production, which requires additional reagents such as sulfuric acid and calcium hydroxide for the pretreatment of the lignocellulosic biomass. On the other hand, scenarios 1 and 2 have similar raw material costs due to these scenarios involve the same amount of reagents for the conversion of the feedstock to synthesis gas and then, the production of hydrogen (scenario 1) and electricity (scenario

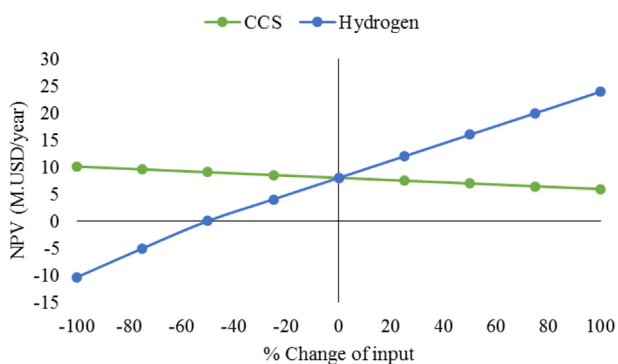


Fig. 11 – Sensibility analysis of the economic performance of the scenario 1.

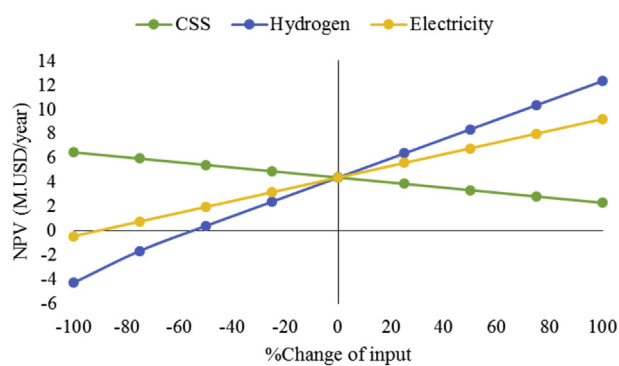


Fig. 12 – Sensibility analysis of the economic performance of the scenario 2.

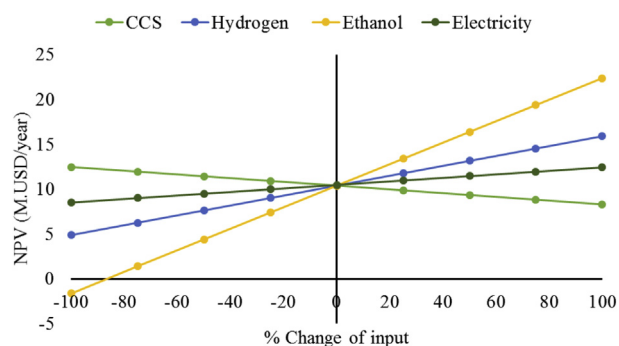


Fig. 13 – Sensibility analysis of the economic performance of the scenario 3.

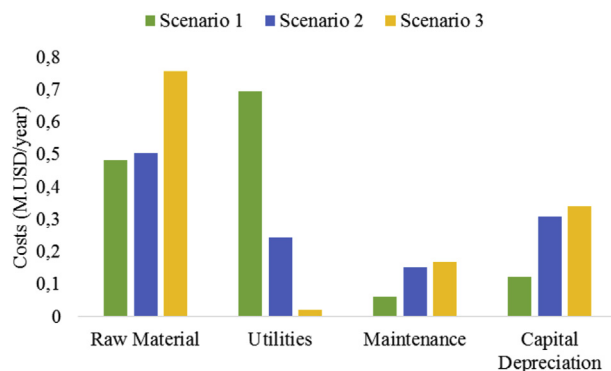


Fig. 14 – Contribution of the economic parameters to the total production costs of the gasification scenarios.

2). Scenario 1 has the highest utilities costs since this process scheme does not consider a cogeneration or power generation plant in order to supply the energy requirements of the synthesis gas conditioning stage prior to the membrane system, which it is a high energy consumption process. In contrast, the utilities costs of the scenarios 2 and 3 are lower than scenario 1 due to the integrated production of electricity from the synthesis gas that would help to meet the energy requirements of the process. The capital depreciation costs were calculated based on the basic sizing of the equipment in each scenario. Scenarios 2 and 3 have the highest capital depreciation costs, which are related to the high direct costs of the

electricity generator (scenario 2) and the additional costs of the ethanol processing plant (scenario 3).

Energy analysis

The net energy balance of the proposed scenarios from the simulation procedure was described using Sankey diagrams as presented in Fig. 15. The inputs of the Sankey diagram are related to the potential energy content of the feedstock and energy requirements. The main products from each scenario, along with other by-products such as steam and electricity, are the outputs of the Sankey diagrams. Additionally, the energy losses of the process, based on the energy balance, are also described in these diagrams. The highest energy exploitation of the gasification scenarios was obtained in the scenario 3 due to the integral production of different bioenergy products under the biorefinery scheme.

The energy efficiency of the scenarios was evaluated based on two criteria: the energy efficiency only considering hydrogen as the main product of each scenario (Efficiency 1)

and the energy efficiency |considering all the bioenergy products (Efficiency 2). Both energy efficiencies of the evaluated scenarios are presented in Fig. 16. When considering only the hydrogen as main product of the scenario, the scenario 1 has the highest energy efficiency due to the direct production of hydrogen from the synthesis gas. Nevertheless, the energy efficiency of the gasification scenarios is very low when considering only hydrogen as main product. As a consequence, the energy efficiency of the scenarios taking into account all the bioenergy products was also calculated, as evidenced in Fig. 17. The energy efficiency of the scenario 1 was improved from 24.96% to 62.06% and the scenario 2 from 12.48% to 58.20%, whereas the energy efficiency of the scenario 3 reached 94% due to the integrated production of hydrogen, ethanol, electricity and steam under the biorefinery scheme.

Additional to the energy efficiency, the relation between the required energy in a process scheme and the amount of produced energy from the main products can be also used as a decision criteria of the sustainability of different process schemes. In this sense, the Net Energy Value (NEV) was used

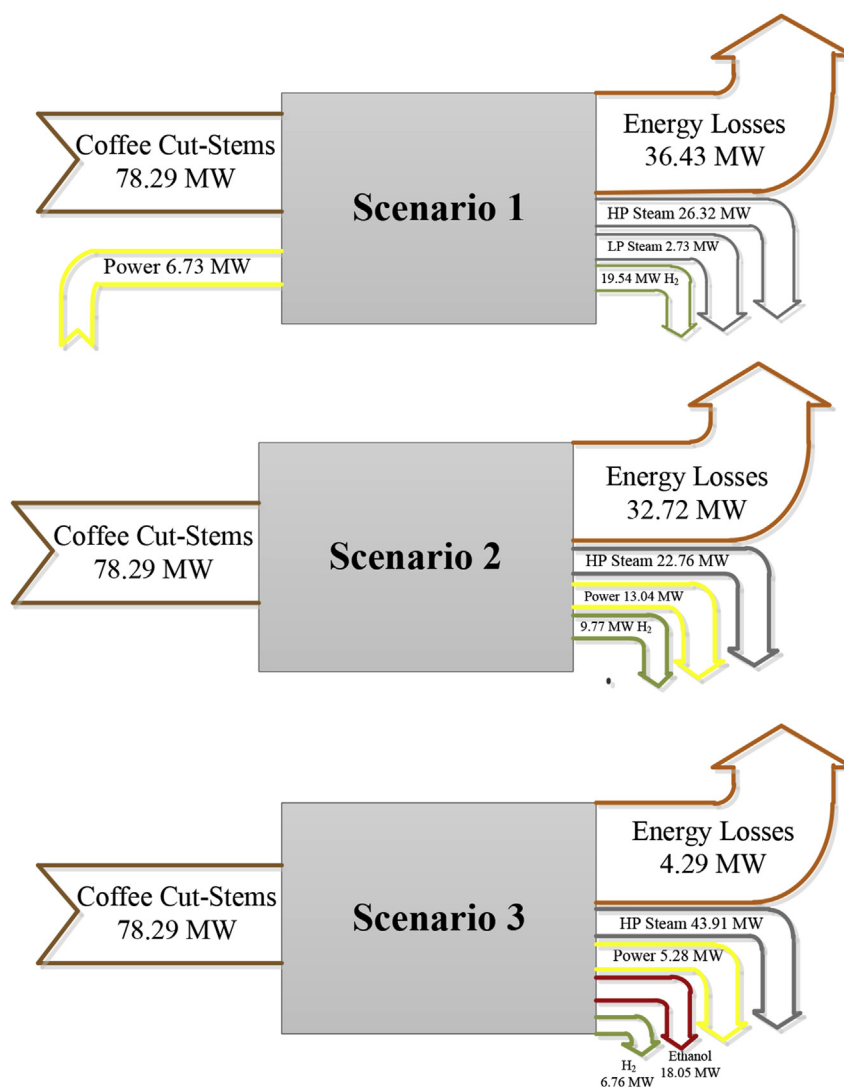


Fig. 15 – Sankey diagrams for the gasification scenarios.

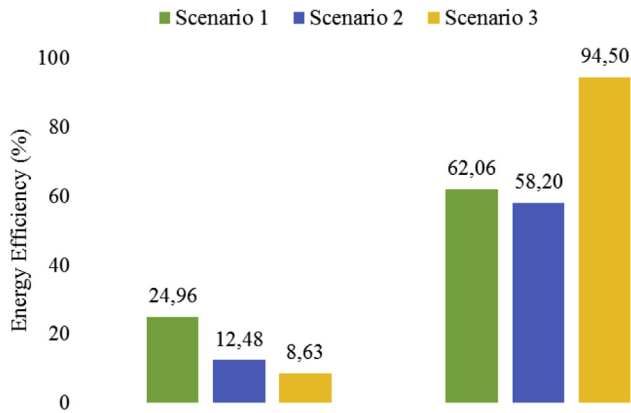


Fig. 16 – Energy efficiency of the gasification scenarios.

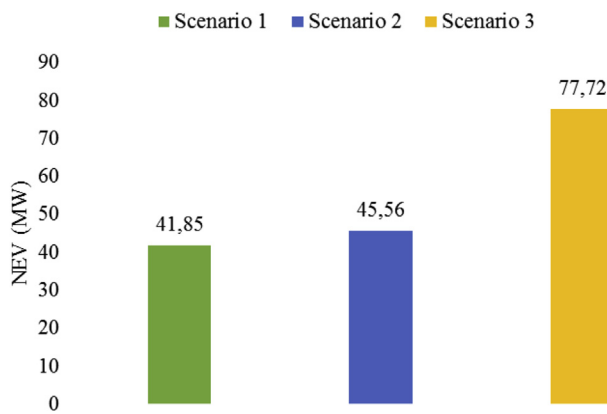


Fig. 17 – Net Energy Value of the evaluated scenarios.

along with the energy efficiency as key parameters in the assessment of the sustainability of the proposed scenarios. Fig. 15 presents the net energy balance of the evaluated scenarios. Positive NEV were obtained from the gasification scenarios, which is related to the high valorization of the bioenergy products in comparison to the energy requirements of the process (see, Fig. 15). The highest NEV of the gasification scenarios was calculated for the scenario 3 due to the lower energy losses and the production of different bioenergy products. From these results, it is noteworthy that the energy efficiency of a process is highly influenced by the implementation of a multiproduct portfolio in the evaluated process scheme.

Conclusions

Coffee Cut-Stems (CCS) is one of the most available wood residues in Colombia that can be used in the production of bioenergy and biochemical products. The high availability and lignocellulosic content of this wood residue evidences its high energy potential in the production of bioenergy multiproduct portfolio. From the pilot-scale gasification, high H₂/CO ratios were obtained; however, additional separation or purification processes are required in order to increase the selectivity of the hydrogen from the synthesis gas. Despite this fact, the

syngas from the CCS gasification can be used in the generation of electricity due to its high energy potential. The techno-economic assessment of stand-alone and biorefinery ways to produce hydrogen evidenced that a multiproduct portfolio enhanced the profitability of the process schemes. The selected products in the biorefinery schemes influenced the NPV of the process. In this sense, low added-value products (i.e. electricity) do not improve the economic performance of the evaluated scenarios. In contrast, high-volume production of ethanol enhanced the NPV of the biorefinery scheme and thus, reduced the hydrogen production costs. Parameters such as the market price variations, products portfolio and the process scale are the most important variables that must be considered to improve the profitability of the hydrogen production. The best scenario for the hydrogen production through gasification was the scenario 3, which considers the production of hydrogen along with ethanol and electricity. The hydrogen production cost, in this scenario, varies between 1.6 and 2.7 USD kg⁻¹. This result is in agreement with the values reported by Parthasarathy et al., [8]. However, the hydrogen production cost should be improved aiming to be competitive to the traditional technologies such as steam methane reforming (SMR) with a production cost of 0.75 USD kg⁻¹. So it is very understandable that the stand-alone ways for hydrogen production are not yet the solution, and different approaches should be included such as the integrated bio-refinery pathways.

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