Experimental production of bioethanol, biogas, syngas and electricity under the biorefinery concept

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Abstract

Energy driven biorefineries can be designed considering biotechnological and thermochemical conversion pathways. Nevertheless, an energy and environmental comparison is necessary to establish the best way to upgrading lignocellulosic biomass and set the requirements of these processes to be applied in different scenarios and scales. In this way, the aim of this work is to evaluate from an energy and environmental perspective the experimental production of energy using CCS as feedstock in two different scenarios, i) bioethanol and biogas through the biorefinery concept and ii) the pilot-scale air-downdraft gasification for the syngas and electricity production. For this, the chemical characterization of CCS in terms of chemical composition, proximate analysis and crystallinity index was done. Then, the experimental production of biogas, bioethanol and syngas was done using lab scale equipment in the case of the biotechnological conversion routes and pilot scale equipment in the case of the thermochemical production of syngas. Thereafter, the energy and environmental analysis was done using a set of indicators to determine aspects such as energy efficiency and environmental impact. The results of both biorefineries leads to establish that the energy-driven biorefinery using biotechnological conversion pathways has a higher energy consumption and environmental impact than the thermochemical route. Therefore, low energy efficiencies and high environmental impacts were obtained. As conclusion from these results, biotechnological processes ought to be implemented at high scales and produce added-value products. Meanwhile, thermochemical conversion using gasification as technology and air as oxidizing agent only can be implemented for energy generation purposes at low and middle scale applications.

Keywords. Biogas, syngas, bioethanol, electricity, energy and environmental analysis.

1. Introduction

The use of fossil fuel to supply the increasing energy demand in the world has been one of the main causes of the environmental issues today. In fact, the excessive use of non-renewable energy sources such as crude-oil, natural gas and coal has caused problems such as global warming and water pollution [1]. Biomass has been postulated as one of the most feasible alternatives to be used as renewable resource to supply a share of the energy demand in the world. In this way, different residues such as sugarcane bagasse, oil palm fronds, *Pinus patula* have been tested as alternatives for energy vectors production. A potential raw material obtained from the coffee crop are the Coffee-Cut Stems (CCS), which are produced during harvesting activities. This residue is a lignocellulosic material able to be processed in thermochemical and biotechnological pathways to produce bioethanol, biogas and syngas. Moreover, CCS have not been widely studied in the open literature and can be profiled as a renewable alterative for decentralized energy production in rural zones, which allows its valorization and use [2]. In this way, the aim of this work is to evaluate from an energy and environmental perspective the experimental production of energy using CCS as feedstock in two different scenarios, i) bioethanol and biogas through the biorefinery concept and ii) the pilot-scale air-downdraft gasification for the syngas and electricity production.

2. Materials and methods

2.1 Raw material and analysis of chemical composition

CCS were obtained from a farm placed at Salamina (N 5° 22' 19.56"O 75° 29' 45.718"), a town of north of Caldas province, located in the center of Colombia. The physicochemical characterization of feedstock was carried out in triplicate and determined using NREL standards (National Renewable Energy Laboratories) for moisture, extractives, ashes calculation. TAPPI (Technical Association of the Pulp and Paper Industry) methodologies were use to determine cellulose, hemicellulose, Klason lignin and soluble lignin content (T-264-cm-07; T-211-cm-93; T-249-em-85) through a quantitative acid hydrolysis with sulfuric acid at 72% (w/w). Initially, moisture content was measured at 105ºC using Shimadzu moisture balance MOC - 120H. Then, CCS were submitted to a soxhlet extraction with ethanol at 70°C, 96% (v/v) and 24h to obtain the extractives content [3]. The solid was dried in an oven at 40°C and 24h. Later, the dried material was submitted to the total ignition in order to determine ashes content [4]. Liquid fraction from quantitative acid hydrolysis was analyzed through High-Performance Liquid Chromatography (HPLC- ELITE LaChrom) to determine the sugars content (glucose and xylose) by a Refractive Index Detector (RID) and a CHO – 782Pb (300mm*7.8mm) Aminex (BioRab) column. Additionally, the liquid fraction was analyzed through UV spectrophotometry in order to determine the furans (furfural and hydroxymethylfurfural (HMF)) content as reported Martínez et al. (2000) [5]. Soluble lignin was predicted through spectrophotometry at 220 nm, where the liquid fraction was diluted in sulfuric acid at 4% (v/v) with a mass ratio 1:20. Solid fraction from quantitative acid hydrolysis was used to determine the Klason lignin content by gravimetry.

The proximate analysis involves four measures, ash, volatile matter, moisture and fixed carbon. The determination of ash content was carried out through the protocol reported on the ASTM D1102 – 84 [6]. The establishment of volatile matter was performed according to ASTM E872 - 82 using a platinum crucible at 950°C and 7min [7]. The moisture content was determined according to ASTM E871 - 82 using a porcelain crucible at 103°C and 24h [8]. Finally, the fixed carbon was estimated as the difference between the ash and volatile matter content on dry basis. Finally, the crystallinity analysis was done to analyze the differences between the raw CCS, pretreated material and the remaining solid from the saccharification process. The crystallinity index defined as the crystalline to amorphous ratio was calculated based on the method proposed by Segal et al., [9].

2.2 Configurations of CCS biorefineries

The description of the stages involved in each biorefinery are indicated in **Figure 1** and explained below**.**

2.2.1 Particle size reduction stages

CCS were sun-dried and cut in slices of 3-5mm of width and 10-30mm of diameter using a Bandsaw (DeWalt DW731). The obtained slices were dried in an oven (Thermo Precision model 6545) at 40°C and 24h. This material was used for the syngas and electricity generation. Then, the slices obtained in the first particle size reduction were milled using a knife mill (Thomas Model 4 Wiley® Mill) adapted with a 2mm mesh. After milling, the material was sieving to pass meshes of 40 (0.425mm) and 60 (0.250mm). A re-milling was necessary in order to have a good amount of material in the meshes mentioned. This material was used for the physicochemical characterization and the production of bioethanol and biogas.

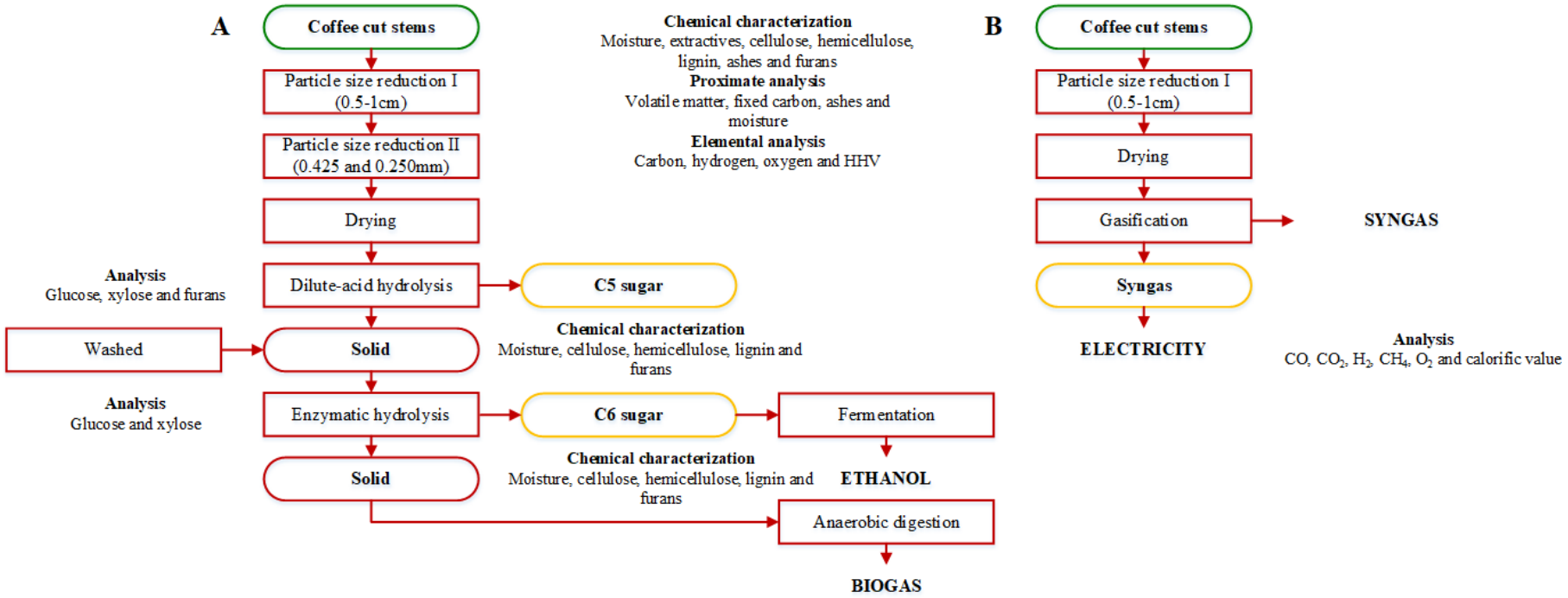

Figure 1. Flowsheet of CCS biorefineries for the experimental production of, A) bioethanol and biogas, and B) syngas and electricity.

2.2.2 Dilute acid pretreatment

Milled CCS samples (25g) were mixed with sulfuric acid at 2% (v/v) to obtain a 1:10 solid-liquid mass ratio in Schott glass bottles of 250mL [10]. Then, vessels were introduced in autoclave (Sanyo MLS – 3781L) under the following operating conditions, 115°C and 3h. When the reaction time was completed, the vessels were cooled until room temperature. At the end of the pretreatment, the solid and liquid fractions were separated by vacuum filtration and solid fraction was characterized to determine cellulose, hemicellulose, Klason lignin and soluble lignin using the procedure mentioned in **Section 2.1**. The acid hydrolysis assays were performed in triplicate.

2.2.3 Enzymatic hydrolysis

The solid fraction obtained in the acid hydrolysis was washed three times to remove traces of reagent used in the pretreatment stage. Then, the solid was dried in an oven at 40°C and 48h, and the moisture content was measured. In an Erlenmeyer of 300mL were putted 14g of dried solid. The enzymatic hydrolysis of cellulose to glucose was carried out with the commercial enzyme Cellic Ctec2 (cellulase), provided by Novozymes (Denmark). The enzymatic hydrolysis assays were performed in an incubator (Binder BD 115- UL) adapted with an orbital shaker (DLAB SK - O330 - Pro) at 50°C and 130rpm, respectively. The enzyme was added considering that Cellic Ctec2 has an enzyme activity of 145 ± 3.19 filter paper units (FPU) per mL and an enzyme dosage of 20 FPU per gram of dried solid in an sodium citrate buffer at 0.05N (pH 4.8). The solid fraction was mixed with the buffer solution at 1:7.5 ratio (% w/v) corresponding to 140g L^{-1}. Samples were withdrawn and analyzed by HPLC to determine the glucose and xylose concentration. Finally, solid and liquid fractions were separated by vacuum filtration. The solid fraction was dried in an oven at 40°C and 48h. Then, this was chemically characterized to perform mass balances. The enzymatic hydrolysis assays were performed in triplicate.

2.2.4 Ethanolic fermentation

The liquid fraction generated in the enzymatic hydrolysis was used as culture medium for the cellular propagation and ethanol production using *Saccharomyces cerevisiae* yeast. Before these procedures, the culture medium was sterilized at 121°C and 15min. The cell growth was the same in a medium with and without nutrients, therefore, the addition of nutrients was not considered in the assays made in this work. It was verified experimentally. Initially, the yeast was adapted to the culture medium in an aerobic environment at 32°C, 180rpm and a volume corresponding to 10% of the total vessel (Erlenmeyer of 300mL). Each propagation was carried out for 24h with continue cell replicate until reach a concentration greater than or equal to $1.7*10^7$ cell mL^{-1} in the fermentation volume. The quantification of cell growth in the propagation and fermentation was performed using Neubauer chamber counting method. Finally, the fermentation process was carried out in an Erlenmeyer of 300mL at anaerobic environment, 30°C, 100rpm and a fermentation volume corresponding to 80% approximately, of the total volume. The pre-inoculum corresponded to the 10% of fermentation volume. Samples were withdrawn between 0 and 24h and analyzed by HPLC and GC-FID for the determination of sugars and ethanol content, respectively. The fermentation assays were performed in duplicate.

2.2.5 Anaerobic digestion

The solid-fraction produced in the enzymatic hydrolysis process was used as the substrate to produce biogas through an anaerobic digestion process. The standard method VDI 4630, published by the Association of Germany Engineers, was applied to set-up the operating conditions of the biochemical methane potential assays (BMP). Indeed, the anaerobic digestion process was done at 37°C during 20 days and using an inoculum to substrate ratio of 0.4 g VS substrate/g VS inoculum. Moreover, the headspace in each assay was about 25%. Sludge from a UASB reactor installed in a wastewater treatment plant located at Chinchiná, Caldas (4°58′50″N, 75°36′27″O), was used

as the inoculum [11]. Airtight glass vessels were used to carry out the anaerobic digestion process. Then, an anoxic atmosphere was ensured using nitrogen. Finally, the biogas production was monitored daily applying the water displacement method. In addition, CH_4 and CO_2 were quantified using a gas analyzer equipment (*i.e.*, Gasboard 3100P, Wuhan, China).

2.2.6 Gasification

CCS were gasified using a 10-kWe pilot-scale air-downdraft gasifier. The raw material was chipped until reaching a particle size from 1.0 to 3.0 cm as pretreatment of this process. Then, the syngas composition was measured using a portable gas analyzer (Gasboard—3100P, Wuhan, China). From this process, the volumetric compositions of O_2, CO, CO_2, H_2, CH_4 and C_nH_m (*e.g.*, ethane and propane) were determined. Finally, the carbon conversion and cold gas efficiency of the process were calculated using the mass balances derived from the equipment. Moreover, a global energy balance was performed using the heating value of the produced syngas and the raw material to identify the energy losses during the process. The electricity production was carried out burning the syngas in a spark gas engine Kubota model DG972 and electrical generator Mecc-Alte ECO3N-4.

3. Results and discussion

3.1 Experimental results

3.1.1 Energy driven biorefinery for the production of bioethanol and biogas

Regard the hemicellulose conversion, the CCS pretreatment allows obtaining a conversion into oligomers and monomeric sugars of 87.38%. This result is comparable with the conversions reported for a wide variety of raw materials such as aspen wood and yellow poplar [12], [13]. On the other hand, the xylose yield of the pretreatment process was 8.29 g/100 g of CCS. This result also is approximate to the reported values for other angiosperm hardwood pretreated by this method. Moreover, other important aspect to consider is the formation of inhibitory compounds. In this process, a furfural concentration of 1.85 g/L was obtained. This result indicates a partial dehydration of xylose product of the hemicellulose. However, the concentration obtained in this experience was comparable with the furfural concentration of hardwoods such as *Eucalyptus globulus* chips at high temperatures (*i.e.*, 140°C – 200°C), low residence times (*i.e.*, 5 – 10 min) and low acid concentrations (*i.e.*, 0.5% - 2.0% w/w) [14]. Finally, the solid recovery in the dilute acid pretreatment of CCS was 61.67%, which is comparable with the results reported for Artichoke stalks [15]. Thus, the operating conditions selected to perform the dilute acid pretreatment of CCS gives goods results in terms of low inhibitory compounds concentration, high xylose production and high-pretreated solid recovery.

The saccharification stage was performed using the remaining solid from the dilute acid pretreatment process. A liquor with a glucose concentration of 14.5 g/L was obtained using Cellic CTec2 as enzymatic cocktail. Nevertheless, the solid characterization before and after only accounts 20% of cellulose conversion. This result is lower than the conversions reported using this enzymatic cocktail [16]. In fact, conversions higher than 60% were reported by Ramos et al., [17] at similar operating conditions (*i.e.*, 150 rpm, 5% total solids, 18 FPU/g substrate). The low cellulose conversion after of hydrolysis can be explained analyzing the crystallinity of the solid before the process. Indeed, the solid used in the saccharification process has a high crystallinity index, which involves a high difficult of the enzymes to degrade the cellulose. This high crystallinity index is explained due to the drying process performed to the solid before the enzymatic hydrolysis. This explanation can be validated due to the crystallinity

index of the pretreated solid is lower than the crystallinity of the raw CCS. Therefore, the solid from the pretreatment process cannot be dried due to the re-crystallization of the cellulose.

The ethanolic fermentation starts with a sugar concentration of 13.020 ± 0.141 g L^{-1}, which at the end of process (24h after) reaches a value of 0.085 ± 0.005 g L^{-1}, namely, that the glucose consumption is of 99.34%. The yield of CCS fermentation is 0.47 ± 0.03 g of ethanol per g of glucose. García et al. (2018) reported various fermentation configurations using S. *cerevisiae* and *Pinus patula* hydrolyzed as microorganism and substrate, respectively. The difference between them, is related to substrate composition. For the fermentation 1, 2 and 3 an experimental yield of 0.368, 0.371 and 0.355 g of ethanol per g of glucose is obtained, respectively [18], after 69h of fermentation. When the obtained and reported results are compared, it is possible to conclude that the fermentation process carried out in this work presents a better performance in terms of sugar consumption and ethanol yield. This result can be attributed to the propagation stage that is considered previous to the fermentation process and is carried out in order to adapted the microorganism to the culture medium and improve its achievement.

The anaerobic digestion process was performed at mesophilic conditions to degrade the remaining solid of the saccharification stage as much as possible to produce biogas. The biogas yield obtained after 20 days was 85 ml/g VS of exhausted CCS. Moreover, the mean compositions of CH_4 and CO_2 were 60.62% and 39.38%, respectively. Therefore, the produced biogas has an energy content in the range of 21 - 24 MJ/m^3. These results are lower than the reported for a wide variety of raw materials [19]. This is because of the remaining solid from the enzymatic hydrolysis process is mainly composed by crystalline cellulose and lignin. In fact, raw materials with high lignin content have low biogas yields due to the complexity to accomplish the degradation of this component. Finally, a theoretical power generation potential of 9.24 kWh/kg biogas can be calculated, which is very similar to the reported electricity potential of the biomass produced by different feedstocks [19].

3.1.2 Energy driven biorefinery for the production of syngas and electricity

The syngas composition produced from the CCS gasification is in terms H_2, CO, and CH_4 was 17%, 13% and 4%, respectively. This result implies a heating value of the syngas of 3.8 MJ/kg. These results are in agreement with the syngas composition reported for different hardwoods and softwoods. Moreover, the syngas composition in terms of H_2 and CO reflects the low range of applications of this gas to produce added-value products. For this reason, electricity production was considered as alternative. The potential of electricity production from the gas is about 5.12 kWh/kg. This value is lower than the obtained in the biogas production case. Nevertheless, high flows of gas are the main advantages of this technology regarding low and middle scale applications. Finally, the yield of the CCS gasification was 1.30 Nm^3/kg of CCS, which is higher than the obtained in the biogas production process.

Regarding energy analysis, the first biorefinery configuration has a high-energy intensity than the second process due to the amount of energy required to maintain the process conditions required in the pretreatment, saccharification, fermentation and distillation stages. Moreover, the carbon conversion efficiency of the process is lower in the first biorefinery because of the carbon losses into the different stages of the process. In fact, the carbon conversion efficiency of the first biorefinery was 62% and the second biorefinery was 97%. Moreover, the second biorefinery has a high renewable energy use due to a share of the produced energy is destined to supply the milling process power requirements. Meanwhile, the first biorefinery needs supply a share of the energy needs using non-renewable energy sources. The environmental assessment leads to establish that the biotechnological production of bioethanol and biogas has more environmental impact caused by the number of waste streams generated in each one of the processing stages involved into the biorefinery. Nevertheless, this configuration leads to obtain more

valuable products (e.g., digestate, gypsum, bioethanol, biogas, xylose liquor) than the second biorefinery. Therefore, this process has a great potential to be applied at higher scales.

4. Conclusions

Lignocellulosic biomass is identified as a potential feedstock to obtain bioenergy. In fact, CCS are a potential feedstock to produce bioethanol, biogas and syngas through the application of biotechnological and thermochemical conversion pathways. The thermochemical conversion of CCS is more energy efficient and environmental friendly than the biotechnological conversion pathway due to the difference in the stages involved in each process. Nevertheless, the thermochemical conversion routes using air-gasification only can be implemented at low and medium scales due to the low heating value of the syngas produced. High thermochemical applications requires the set of a co-gasification system or the use of another oxidizing agent. Respect to the biotechnological conversion routes, these ones are more feasible from the economic perspective than the thermochemical facilities. Nevertheless, a limit in the energy and environmental aspects must be fixed to guarantee a low impact in terms of releases and non-renewable energy sources consumption.

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