Comparison of processing lines to convert lignocellulosic C5 sugar platform to furfural and biogas

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Abstract

Purpose. To compare two stand-alone processes for the valorization of C5 fraction from Coffee cut-stems (CCS) and production of biogas or furfural. What will be the best process option from technical, economic and environmental point of view?

Methods. CCS were used as feedstock for the experimental production of biogas and furfural under stand-alone concept. The experimental results were translated to simulation procedures in order to compare the cases in technical, economic and environmental terms. The technical aspect is analyzed based on the productivities and energy consumption. The economic component is assessed according to production costs and Net Present Value (NPV) vs processing scale of raw material. Finally, the environmental perspective is analyzed using Life Cycle Assessment (LCA) methodology with a cradle-to-gate approach.

Results. The experimental results are the base to the simulation of both process schemes. From technical point of view, the biogas production presents lower energy requirements than furfural production, making this processing line attractive.

Conclusions. In general terms, the C5 sugars platform is identified as potential alternative for the generation of added-value products. From environmental point of view, this work concludes that for bio-based processes it is necessary and relevant the inclusion of the feedstock production because this system can positive or negative contributions in the impact categories.

Keywords. Lignocellulosic biomass, xylose platform, furfural, biogas, stand-alone processes.

1. Introduction

In biomass processing the variety of products requires in many cases the comparison of alternatives. Platforms based on C5 hemicelluloses are processed and can be compared as stand-alone processes for the valorization of these fractions. The C5 fraction from CCS can be analyzed for the production of biogas or furfural. At this point, the question is what will be the best process option from technical, economic and environmental point of view. In the present work, CCS were used as feedstock for the experimental production of biogas and furfural under stand-alone concept. The experimental results were translated to simulation procedures in order to compare the cases in technical, economic and environmental terms. The technical aspect is analyzed based on the productivities and energy consumption. The economic component is assessed according to production costs and Net Present Value (NPV) vs processing scale of raw material. Finally, the environmental perspective is analyzed using Life Cycle Assessment (LCA) methodology with a cradle-to-gate approach.

2. Materials and methods

2.1 Raw material

CCS were obtained from a farm placed at Salamina, a town of north of Departamento de Caldas, 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 used 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 [1]. 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 [2]. 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. Type I water was used as mobile phase. The column oven and RID were maintained at 80ºC and 45°C, respectively. The flow rate for mobile phase was fixed at 0.6 ml min^{-1}. The polysaccharides (cellulose and hemicellulose) content was estimated using the obtained HPLC data. The samples analyzed by HPLC were previously centrifuged (Sprout mini centrifuge), filtered and diluted. The filtration was carried out using nylon membranes (syringe filter: 0.22μm of pore and 25mm of diameter). Additionally, the liquid fraction was analyzed through UV spectrophotometry in order to determine the furans (furfural and hydroxymethylfurfural (HMF)) content following the protocol reported by Martínez et al. (2000) [3]. 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.

2.2 Stand-alone processes

In this work, two stand-alone processes were considered for the experimental production of biogas and furfural using CCS and C5 sugars as feedstock and platform, respectively. **Figure 1** shows the flowsheet of both processes in its experimental setup. A description of each process is presented below.

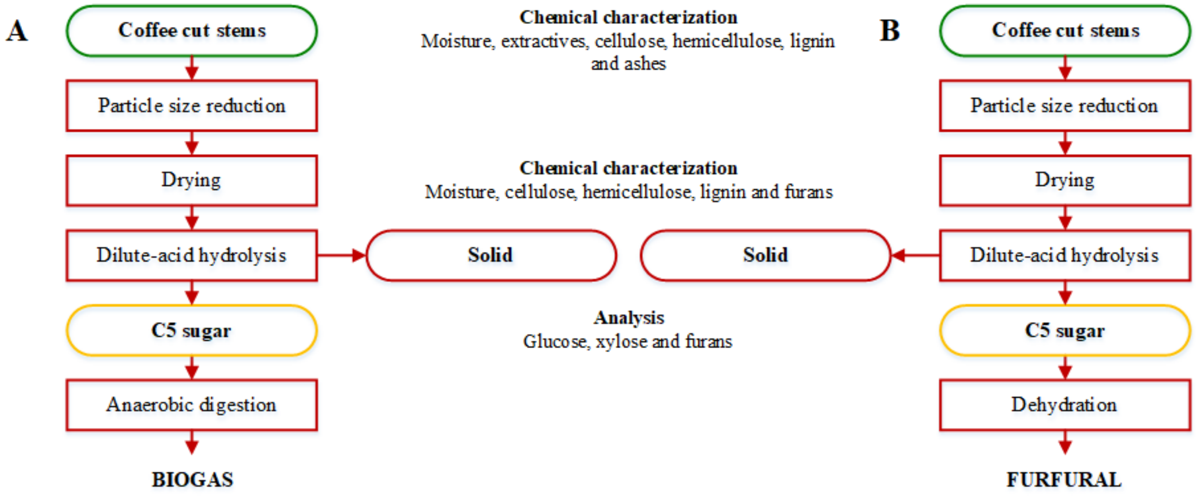


Figure 1. Flowsheet of stand-alone processes for the obtaining of, A) biogas and B) furfural.

2.2.1 Particle size reduction

CCS were sun-dried and cut in chips0.5-1.0cm using a Bandsaw (DeWalt DW731). Then, these chips 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). The obtained material was dried in an oven (Thermo Precision model 6545) at 40°C and 24h. This material was used for the physicochemical characterization and the production of biogas and furfural.

2.2.2 Acid hydrolysis

Milled CCS sample (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 [4]. 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. The liquid fraction contents xylose, which was used as platform to produce furfural or biogas in two different process configurations.

2.2.3 Anaerobic digestion

The C5 sugars fraction generated in acid hydrolysis was used as substrate in the anaerobic digestion for the biogas production at 37°C, 25 days and a pH of 7.0 in a thermostatic bath using as inoculum, sludge from spent coffee grounds [5]. The pH value was adjusted with NaOH 5M. The digestion was carried out in airtight glass vessels with an initial nitrogen purge and the mixed of substrate and inoculum covered the 75% of total volume of vessel. The liquor and sludge load to the vessel was calculated using experimental data for volatile solids (VS) and total solids (TS), which was determined using the Standard methods 2540 [6]. It is necessary to guarantee that the inoculum provides between 7.5-10 g of VS per 500mL of digestion volume [5]. Angelidaki et al. (2009) indicated the supplementary chemicals for the culture medium [7], which were added according to the relations presented by the German standard VDI 4630 [5]. Per 100ml of digestion volume 1 and 0.4ml of macronutrients and micronutrients solution were used, respectively. The productivity monitoring was conducted with displacement of water volume for the gas. The biogas composition was measured using a portable gas analyzer (Gasboard—3100P, Wuhan, China), which records the volumetric composition of CO_2, and CH_4. The anaerobic digestion assays were carried out in duplicate.

2.2.4 Dehydration

The liquid fraction obtained in the acid hydrolysis was taken to produce furfural through a dehydration reaction catalyzed by chromium (III) chloride ($CrCl_3$), in a molar ratio of 0.06 respect to the sugars. The operating conditions were, 180°C and 11bar for 2h [8]. A HP-Autolab Reactor with a maximum capacity of 300mL was used to carry out the reaction. The work volume was the 30% of the maximum capacity. The compounds such as NaCl and HCl were added to the reactor in order to improve the reaction performance. NaCl corresponded to that needed to saturate the water (35 g of NaCl per 100 g of H_2O) and HCl was 0.12 mol L^{-1} [8]. For reaching to work pressure, nitrogen gas was used. At the end of the dehydration, the HCl was neutralized with NaOH at 80°C per 10min. Samples were withdrawn at the beginning and end of the reaction and analyzed by HPLC and UV/Vis spectrophotometry for the identification of sugars and furans content, respectively. The dehydration assays were conducted in triplicate.

2.3 Technical, economic and environmental assessment

For the two proposed process configurations, mass and energy balances were experimentally obtained and then translated to simulation procedures. The commercial package Aspen Plus (Aspen Technology, Inc., USA) was used as the main simulation tool. Non-random two-liquid (NRTL) thermodynamic model was selected to calculate the activity coefficients of the liquid phase, and the Hayden-O'Connell equation of state is used for describing the behavior of the vapor phase. The energy consumption was determined using Aspen Energy Analyzer v9. The software Aspen Process Economic Analyzer v9 was used to calculate the capital and operating costs. This analysis was estimated in US dollars for a 10-year period at an annual interest rate of 17% (typical for the Colombian economy), considering the straight-line depreciation method and an income tax of 25%. For this purpose, a base plant capacity (amount of CCS) of 234 tons per day (according to availability of CCS in Colombia) was selected and the effect of different capacities (50, 108 and 180) in the economic profitability (*i.e.*, production cost of the main product in each configuration) was evaluated. Based on this analysis, the contribution of the main economic parameters as CAPEX (based on fixed capital costs of equipment), OPEX (calculated as the sum of costs of raw materials, utilities, maintenance, labor, fixed and general costs and overhead) and the general profits from the product were plotted together [9].

Life-cycle assessment (LCA) is a methodological tool used widely to measure and quantify the environmental impact of a product, service or process throughout its life cycle (from the raw material production until the process end life) [10]. This methodology aims to identify the main environmental *hotspots* of the evaluated processes [11], [12]. The software SimaPro v8.3 (PRe Sustainability, Netherlands) and the Ecoinvent database were used to measure the environmental impact of the cradle-to-gate approach that includes the CCS production (germination, nursery, site preparation, stage of vegetative growth, production stage, cutting and transport) as well as the production of biogas and furfural two stand-alone processes. The impact assessment of the processes was performed using the characterization method of ReCiPe Midpoint (H - hierarchist version) v1.13. Climate change (CC), Freshwater eutrophication (FE), Human toxicity (HT), Freshwater ecotoxicity (FET), Agricultural land occupation (ALO), Water depletion (WD) and Fossil depletion (FD) were some categories involved. The generation of 1 kilogram (kg) of product was chosen as the functional unit. Meanwhile in the CCS production, a functional unit of 1 ha of coffee was selected [13]. From the simulation made in the Aspen Plus computer tool, the mass and energy balance were taken as input and output data for each process. A detailed inventory of the CCS production was used, based on data reported by Federación Nacional de Cafeteros de Colombia and Centro Nacional de Investigaciones del Café (Cenicafé) [13].

3. Results and discussion

This section comprises the results and discussion of the experimental work, technical, economic and environmental analysis.

3.1 Experimental results

The experimental results involve physicochemical characterization of CCS, yields and conversions of dilute-acid hydrolysis, production of furfural and biogas. **Table 1** shows the physicochemical characterization of CCS, which is compared with the results reported by other authors. As can be seen, the most of components have similar values, which validate the characterization procedure used. However, hemicellulose and lignin present significant differences that can be influenced by factors such as the location of the coffee crop, the climate, crop management, time and manner of storage, among others. High amounts of lignin content hinders the access to hemicellulose and cellulose polymers, therefore, to their monomers (*i.e.,* xylose and glucose). The lignin is presented as a barrier that gives resistance and rigidity to the structure of the material. This phenomenon can affect the correct action of a pretreatment process and reduce the concentration of pentose monomers.

Table 1. Physicochemical characterization of CCS (% w/w dry).

Component	This work	Quintero et al. (2013) [14]	Aristizábal et al. (2015) [15]
Moisture	9.11±0.39	4.12	11
Extractives	9.36±0.12	8.38	14.18±0.85
Ash	0.96±0.13	2.27	1.27±0.03
Cellulose	35.13±0.81	37.35	40.39±2.20
Hemicellulose	11.42±0.31	27.79	34.01±1.20
Klason lignin	23.27±0.25	19.81	10.13±1.30
Soluble acid lignin	10.74±0.88		

In this work, the CCS are submitted to a dilute-acid pretreatment where a rich-sugars liquor, specifically pentoses, is obtained. These sugars are the building block product for the production of biogas or furfural. The liquor is analyzed by HPLC in order to determine the xylose and glucose concentration and know the start point of anaerobic digestion and dehydration reaction. **Table 2** indicates the yields and conversions obtained in each process stage, acid hydrolysis, and production of biogas or furfural. As can be seen, the pretreatment is considerably effective for the hemicellulose conversion to xylose and furfural, with a value of 97.57%. In the case of cellulose, the conversion is 25.17% to glucose and HMF. The xylose and glucose are the most desired products; meanwhile, the furfural and HMF in this stage are not convenient compounds when the liquor is used as substrate for a fermentation. The furans compounds act as inhibitors to the microorganism [16]. Despite the high lignin content in the CCS, the acid hydrolysis fulfill with its target, that is to release sugars contained in material structure, specially, xylose from hemicellulose with a yield of 0.75 (*see,* **Table 2**).

In the anaerobic digestion, data of SV and TS are needed to calculate the load of sludge and liquor and analyze the results. For the sludge and CCS hydrolyzed, the VS determined experimentally is, 5.93±0.27 and 4.68±0.26 % w/w dry, respectively, meanwhile, the TS is 6.41±0.23 and 4.93±0.17 % w/w dry, respectively. The VS content can be used as a primary indicator for biomethane potential, as a greater content leads to a higher biogas productivity. However, variations in the organic matter composition affect the specific methane yield and make it variable. An important parameter in anaerobic digestions is the biodegradability index (BI), calculated as the ratio between VS and TS of the substrate. This value indicates the opportunity to use a material for biological processes. The BI of the CCS hydrolyzed corresponds to 95%, which in turn explains the possibility to biodegrade substrates from the total VS content when is compared to others materials [17]–[20]. The anaerobic digestion of CCS hydrolyzed, using dilute-acid pretreatment, present a yield of 81.15 mL accumulated CH_4/g VS (*see,* **Table 2**). Kaparaju et al. (2009) performed assays of the biological methane potential (BMP) at thermophilic conditions of 55°C from wheat straw hydrolysates obtained from hydrothermal pretreatments [21]. For this configuration, a methane yield of 384 ml/g VS for feed liquor concentrations of 4.25 and 8.5 g VS/L (there is not a significant difference in yield for other feed concentrations) is obtained. On comparing both values, it is possible that the difference between yields is due to the feed ratio of substrate and inoculum in terms of VS (8.8 g substrate/g inoculum) and the considerable concentration of inhibitory compounds (*i.e.*, furans) in the hydrolyzed.

The CCS hydrolyzed presents a slight concentration of furan compounds that for the dehydration reaction are not considered in the calculation of conversions and yields. In this work, conversions of glucose and xylose of 73.8 and 63% are obtained (*see,* **Table 2**), respectively. Martin and Grossman (2016) presented the furfural production using the same process configuration that in this work, and reported a conversion of 82 and 70% for glucose and xylose, respectively [8]. As can be seen, the values are very close between them, corroborating the experimental assays results from different raw material.

Table 2. Experimental yields and conversions obtained in the process units.

Process unit	Yield	Units	Conversion
Dilute-acid hydrolysis	0.75	g xylose/g HE	HE: 97.57%
	0.12	g furfural/g HE	
	0.06	g glucose/g CE	CE: 25.17%
	0.09	g HMF/g CE	
Biogas	509.50	mL accumulated biogas/g VS	N.R.
	81.15	mL accumulated CH_4/g VS	N.R.
Furfural	0.07	g furfural/g xylose	Xylose: 63%
	0.66	g HMF/g glucose	Glucose: 73.8%

HE: hemicellulose. CE: cellulose
N.R. Non-reported

Figure 2 indicates the biogas and methane production over time using CCS hydrolyzed. In biogas production there are four stages, namely, hydrolysis, acidogenesis, acetogenesis and methanogenesis. As can be seen, biogas formation occurs from the beginning of the process, which indicates that hydrolysis step was not performed due to the simple sugars presented on the liquor substrate. As there is not presence of sugar-polymers, a high biogas productivity can be reached in early stage digestion. For the first five days of assay, an average of specific biogas rate is 31.3 mL $gVS^{-1}day^{-1}$, being the maximum productivity. In contrast, at the end of digestion the biogas rate reached 20.4 mL $gVS^{-1}day^{-1}$. In spite of having a small productivity, it was decided to stop the tests because the substrate is almost depleted. On industrial aspects, it is preferred to obtain higher amounts of biogas using new substrate compared to a material with low carbon source.

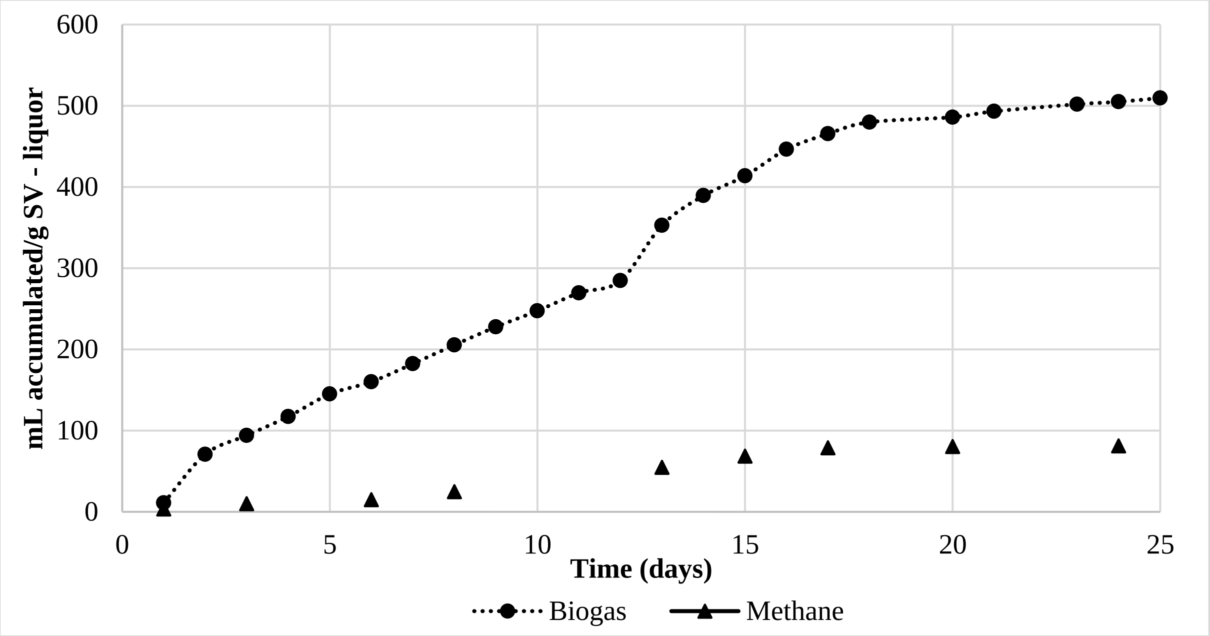
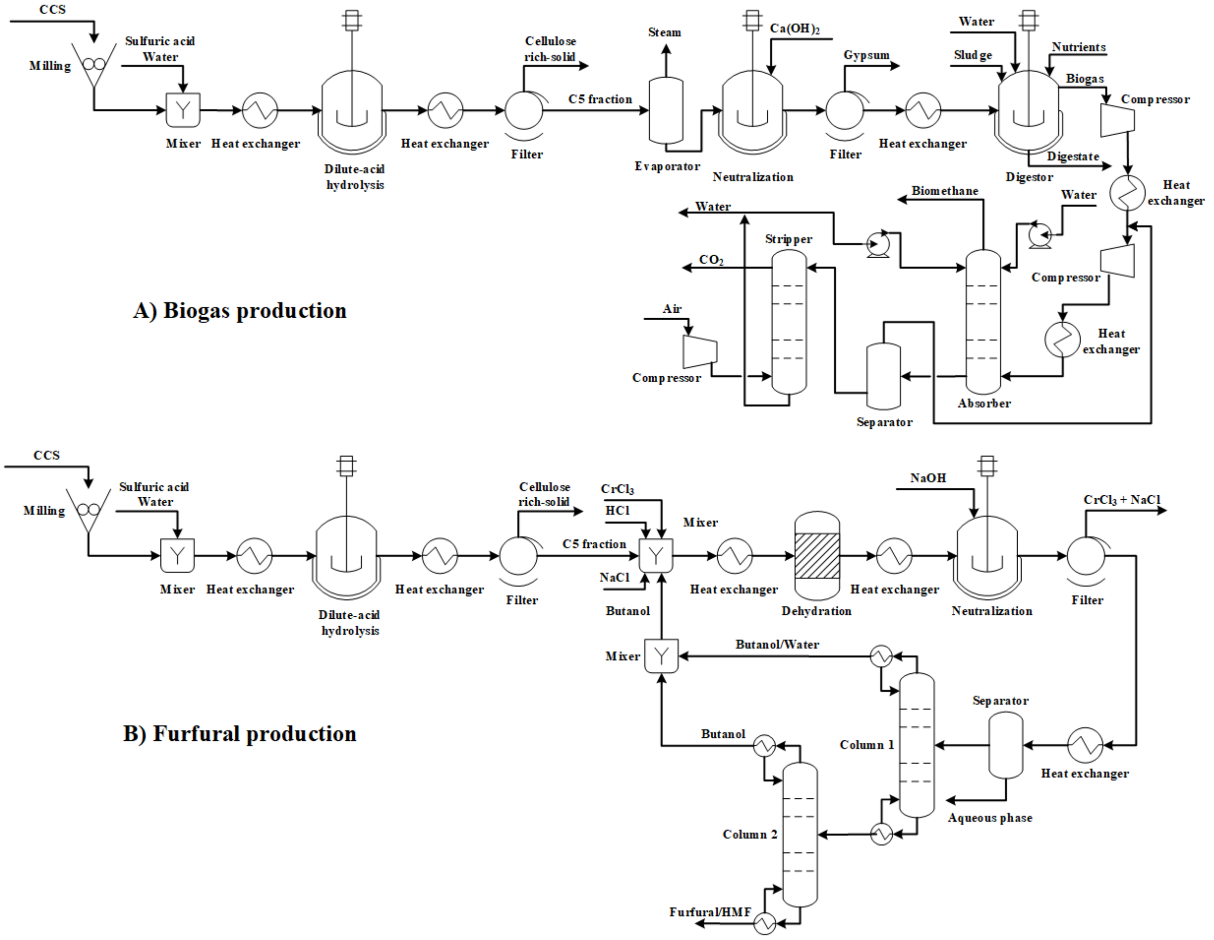


Figure 2. Experimental production of biogas and methane over time using CCS hydrolyzed as substrate.

3.2 Technical results

The experimental results are fed to simulation, where it is supposed that the yields for experimental scale behaves similar to high processing scales. **Figure 3** shows the process schemes for the production of biogas and furfural. From experimental perspective, the biogas and furfural production is carried out until reaction stage. Meanwhile, from simulation point of view, a complete process is considered with pretreatment, reaction and separation stages. Biogas and furfural purification is performed by high pressure water scrubbing technology and distillation technologies, respectively [8], [22]. The technical performance is analyzed based on the energy requirements of process units that compose each configuration. **Table 3** indicates the energy requirements (*i.e.,* cooling water, low pressure steam (LPS), medium pressure steam (MPS), high pressure steam (HPS) and electricity) of both processes. As can be seen, the furfural process has a higher energy demand than the biogas process. This result is linked to the operating conditions of dehydration reaction and the using of two distillation columns for its purification. Although, the biogas scheme also presents a significant energy requirement due to neutralization reaction of sulfuric acid present in the liquor, sugars concentration and refrigeration system for gas compression. In economic terms, the utilities cost is of 60.88 and 31.95 M-USD y^{-1} for the furfural and biogas process, respectively.


A) Biogas production

B) Furfural production

Figure 3. Process schemes A) Biogas production and B) Furfural production.

Table 3. Energy requirements of both processes.

Utility	Biogas (MJ kg^{-1} CCS)	Furfural (MJ kg^{-1} CCS)
Cooling water	1.084	2.247
Low pressure steam	20.55	N.A.
Medium pressure steam	0.009	0.009
High pressure steam	N.A.	3.021
Electricity	0.015	0.008

N.A. Non-Apply.

4. Conclusions

In general terms, the C5 sugars platform is identified as potential alternative for the generation of added-value products. From environmental point of view, this work concludes that for bio-based processes it is necessary and relevant the inclusion of the feedstock production because this system can positive or negative contributions in the impact categories.

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