Economic and environmental analysis of implementing hybrid renewable energy systems (HRES) for heat and power supply in biorefineries.

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Extended Abstract.

Biorefineries are complex systems guided to obtain several products, including chemicals, high-value-added products, biofuels, and bioenergy, after a comprehensive biomass conversion based on mature technologies and a sustainability framework [1]. Novel designs and biorefinery configurations are being developed considering new know-how, raw materials, and technological advances. Today, several large-scale biorefineries are transforming different feedstocks into value-added products with applications in the food, feed, cosmetic, pharmaceutical, nutraceutical, and chemical industries. Nevertheless, new designs and existing large-scale biorefineries still depend to some extent on fossil fuel consumption to supply a share of the heat and power demand to accomplish the desired biomass conversion. Alternatively, the energy matrix of biorefineries (and the industrial sector) still relies more than 60% on fossil fuels [2]. Therefore, the research and engineering efforts must be addressed to analyze the way to supply the energy demanded by biorefineries using several renewable energy sources.

Energy matrix diversification using renewables is an alternative to strengthen and ensure heat and power supply in biorefineries while decreasing fossil fuel dependence and carbon footprint. Then, industry energy matrix diversification can be accomplished by testing, analyzing, and implementing the so-called Hybrid Renewable Energy Systems (HRES). These systems are designed to supply energy using only renewables such as biomass, wind, and sunlight [3]. However, most HRES-related studies have been focused on electricity generation in decentralized zones leaving aside the high potential to decarbonize the industrial sector. Moreover, HRES have not been assessed considering in-depth environmental criteria since most research studies are guided to technical and economic aspects. Lastly, there are no studies until the author's knowledge combing and assessing the design of a biorefinery and HRES. In this way, the joined biorefinery and HRES design and assessment are worthy of research and study since there are many biomass biorefining options as HRES configurations. Thus, HRES must be tailor-made to supply the heat and power demand of a specific biorefinery minimizing the use of fossil fuels and increasing process sustainability. Biorefineries location plays a key role to define the main components of the HRES system since weather conditions vary constantly.

Levulinic acid (LA) has been considered as a chemical platform due to the high versatility to produce other value-added products for the coatings, plasticizers, fertilizers, fuels, and chemical industries [4]. For instance, levulinic acid can be upgraded into levulinates as coalescing agents in water-based coatings and fuel additives. Moreover, this platform molecule can be upgraded into succinic acid, 5-nonanone, and γ-valerolactone. This platform molecule can be produced from glucose, fructose, sucrose, and xylose, which can be found in agricultural waste biomass. The most important producers of levulinic acid are located in North America, Europe, and Asia. Several research studies have been published related to the production of LA using different biomass sources [5]. Nevertheless, the LA demand has been increasing in other world regions such as South America and the transport cost from far sea ports increase the price of this compound. Therefore, the analysis of LA production using lignocellulosic from this region, as well as the techno-economic and environmental assessment based on specific context conditions should be done. Moreover, levulinic acid can be combined with the biorefinery concept since several value-added products are obtained from biomass. In this regard, a biorefinery addressed to upgraded biomass into LA and other products is welcome. Regarding the above context, this research is aimed to design and assess the techno-economic and environmental performance of a biorefinery system coupled with different HRES configurations using renewables such as sunlight, and biomass. In fact, a model biorefinery is proposed and the energy matrix is changed by proposing different HRES configurations to supply the energy demand. The novelty of this research relies on the comprehensive design and analysis of several HRES by combining process engineering concepts and software tools. The biorefinery was designed considering the levulinic acid, ethyl-levulinate, and butyl-levulinate production as main products with an HRES using biogas and sunlight as energy sources. Two raw materials were compared to elucidate the best option. The raw materials were cocoa pod husk (CPH) and avocado seeds (AV). Experimental data, kinetics, and yields were used to simulate the biorefinery configurations and HRES.

The methodology to accomplish the objective involved experimental procedures related to levulinic acid and biogas production using CPH and AV. The model biorefinery was simulated using the experimental yields of the levulinic acid production, while the ethyl levulinate and butyl levulinate production were simulated using kinetics reported in the open literature. A model biorefinery means a case study to apply the different HRES configurations. Nevertheless, the methodology applied can be extrapolated to other biorefineries. On the other hand, a share of the raw materials (i.e., CPH and AV) was used as input to the HRES system. The biomass was converted into biogas through an anaerobic digestion process (AD) in the HRES. The biochemical methane potential (BMP) assay was conducted to find the biogas production yields of these raw materials and the methane content. Moreover, the HRES system involved a solar PV system. The biorefinery and the biogas production processes were simulated using the Aspen Plus software, while the HRES was simulated using the HOMER PRO software. Afterward, technical indicators were estimated to compare the biorefinery couple HRES scenarios to elucidate the best process configuration and raw material. Then, an economic analysis was done to determine the process feasibility based on the value of investment indicators (e.g., net present value, levelized cost of energy, and turnover ratio). Finally, a life cycle assessment (LCA) was done to elucidate the environmental performance of the biorefineries coupled with HRES. The SimaPro software v.8.3.3 was used to estimate midpoint indicators such as climate change, ozone depletion, fossil depletion, and water acidification. In summary, the process, experiments, simulation approach, and assessment methodologies are described.

Model biorefineries were addressed to produce levulinic acid and derivatives (i.e., ethyl levulinate and butyl levulinate). The heat and power required to supply the energy demand of the process was supplied by the HRES system where a part of the raw material input was destined for biogas production. Moreover, sunlight was used as another energy source in the HRES system. Levulinic acid production was carried out by the homogenous dehydration of the raw material using sulfuric acid as an acid agent. The process configuration was done based on previous literature reports [4,6]. The biofine technology was applied to produce levulinic acid. Thus, the operating conditions (i.e., temperature, acid concentration, and catalytic conversions) were carried out according to the GF Biochemicals Patent [7]. The LA purification process was done using conventional technologies such as liquid–liquid extraction and distillation. Methyl-isobutyl ketone (MIBK) was used as a solvent to separate LA from the aqueous solution after the reaction. Then, the LA is recovered by distillation as the bottom product. Then, MIBK and formic are recovered. Afterwards, 60% of the levulinic acid was sent to an esterification process to produce derivatives. The kinetics of the esterification process were retrieved from the literature. Finally, a sequence of distillation columns was proposed to separate the desired products.

Cocoa Pod Husk (CPH) and Avocado Seeds (AV) were used as raw materials. The raw materials were characterized in terms of cellulose, hemicellulose, lignin, ashes, extractives, and moisture. Standard methods were used to determine the content of each fraction. CPH were collected in the Meta, Colombia. Meanwhile, the AV were collected in Sucre, Colombia. Both raw materials were dried and milled to homogenize the particle size. The levulinic acid production was done using fifteen grams (15 g) of AV and CPH were weighed and mixed with 150 ml of distilled water to accomplish the LA production. Sulfuric acid was added to the mixture until pH 2.0. Then, the process was carried out in a pressurized reactor (HP AutoLAB Digi-Plate with Direct Agitation – E-1823S, HEL group) with temperature and stirring control. The operating conditions were 150°C, 10 bar, 200 rpm, and 2 h [8]. Literature was used to estimate the conditions mentioned above. Afterward, the resulting solution was centrifugated at 3500 rpm (Electronic centrifuge LC-04S) for 20 minutes. Then, the liquid was stored at 4 °C until analysis by the DNS method (reducing sugars determination) and HPLC. Finally, the levulinic acid quantification process was done using an HPLC (LC-2010AHT, Shimadzu) and a C18-Kromasil column. An isocratic method was established to analyze the levulinic acid production process samples. The mobile phase was a water mixture: acetonitrile 97:3 (v/v) (both solutions were modified with 0.1% formic acid). The mobile phase flow, injection volume, and wavelength were set at 0.6 ml/min, 20 µl, and 280 nm [9,10]. On the other hand, biogas production was carried out using CPH and AV. The inoculum was an anaerobic sludge obtained from a wastewater treatment plant of a company located in Caldas, Colombia. The volatile solids ratio between the substrate and inoculum was fixed at 0.4 to complete a digestion volume of 100 ml. The BMP test was carried out at mesophilic conditions (i.e., 35°C) for 15 days. The biogas volume was measured by the volumetric displacement method, while the methane content was analyzed using the GASBOARD 3200P portable analyzer.

The biorefineries were simulated using the Aspen Plus v.9.0 software. All simulations were completed considering the Non-Random Two Liquids (NRTL) and Peng-Robinson equation of state (PR EoS) to calculate the activity coefficients and fugacity since high temperatures and pressures are involved in the simulation. Finally, the thermodynamic properties of cellulose, hemicellulose, lignin, and starch reported by the NREL were used to complete the input data in the simulation process. On the other hand, the HOMER software was used to model the most important components of the HRES. This software was developed by the NREL. This software offers advantages since sizing and costing of the HRES system can be calculated based the PV-panels database and the possible specification of the anaerobic digestion system. The HOMER software was selected among other software since HOMER can be used to determine the contribution of each source of energy based on a multiparametric analysis. Thus, integrated energy systems can be proposed based on the best results of the HRES system. The input information was related to the electricity demand, type of PV-panels, project location, and biogas production process. At the end, the HOMER software estimates technical and economic information related to the HRES. Indicators such as the levelized cost of energy (LCOE) was calculated [11].

The economic assessment was done using the Aspen Process Economic Analyzer v.9.0 software and quotations done for some equipment. Mass and energy balances were used as input data. The economic analysis was focused on estimating (i) Capital Expenditures (CapEx) and Operational Expenditures (OpEx), and (ii) value-of investment indicators (e.g., Net Present Value – NPV and Payback Period (PBP)). The methodology reported by the Towler and Sinnot was applied to made the economic assessment [12]. The environmental life cycle assessment (E-LCA) of proposed biorefineries was done by applying the methodology proposed by ISO 14040 and ISO 14041. The E-LCA methodology involves four steps (i) goal and scope definition, (ii) environmental life cycle inventory, (iii) environmental life cycle evaluation, and (iv) results interpretation. First, the goal and scope definition were done to establish the system boundaries, functional unit, and the main assumptions considered in the analysis. Then, the life cycle inventory is completed using primary and secondary information sources. Then, the life cycle assessment is done considering all the impacts caused by the inputs and outputs of the process under analysis. Finally, the results interpretation is done involving midpoint impact categories. The SimaPro v.8.3.3 software was used to perform the analysis.

The results were classified in experimental and simulation results. The chemical characterization of CPH and AV is presented in **Table 1.** The AV have a high C_6-sugar source since starch and cellulose can be upgraded into levulinic acid.

Table 1. *Chemical characterization of CPH and AV.*

Item (%w/w)	**Creole avocado seed**	**Cocoa Pod Husk**
Chemical characterization		
Moisture	13.17 ± 0.093	11.09 ± 0.06
Total extractives	26.45 ± 2.521	30.78 ± 0.74
Fats	9.81 ± 0.257	13.89 ± 0.54
Cellulose	13.38 ± 0.451	21.64 ± 1.267
Hemicellulose	9.30 ± 0.215	15.04 ± 0.058
Total lignin	7.78 ± 0.981	9.95 ± 1.078
Starch	24.58 ± 0.632	1.60 ± 0.80
Ashes	2.86 ± 0.101	3.27 ± 0.11

AV were the best raw materials to produce levulinic acid since the yield after the reaction process was higher. Indeed, the liquor after the reaction process was 143 mL without solids separation. The remaining solid was oven-dried over night to measure the total solids content. The remaining solids had a total solids content of 14.29%. Then, the total mass of solids produced was 2.85 g. The solid residue can be attributed to the generation of carbonaceous material (i.e., Humins). The humins yield was 40.82% (i.e., 26.79 g of humins per 100 g of avocado seeds). This yield is in the range of literature reports giving a humins yield between 15% - 40%. On the other hand, the levulinic acid concentration in the liquor was 7.76 g/L and 5.42 g/L for AV and CPH, respectively. Then, the mass of levulinic acid produced was 1.11 g and 0.84 g. The levulinic acid production yield was 17.98% and 12.36% w/w based on the total C_6 source (i.e., cellulose and starch). The levulinic acid yield involving the initial mass of AV and CPH was 33.01% w/w and 24.12%. These yields are in agree with other values reported in the open literature. For instance, levulinic acid yields from 7.1%, 47.5%, 55.8%, and 66% for cotton residues, woody biomass, sugarcane bagasse, and chickpea (*Cicer arietinum*) have been reported [8].

The specific energy consumption of the biorefinery using AV as raw materials consumes more energy than the CPH due to the low C_6 source. Indeed, the specific energy consumption of the biorefinery was 6.45 MWh/day. This energy can be supplied by a HRES consuming about 28% of the total raw material input. The solar-PV system provides about 56% of the total power required by the biorefinery. Thus, two biogas engines are required. On the other hand, the environmental performance of the process was better using AV as raw material. The HRES is capable to provide 100% of the energy demand of a biorefinery decreasing the fossil fuels consumption. Then, this alternative is profitable to promote decarbonization practices at conceptual design level and industrial level. Regarding the economic performance, the energy supply accounts 12% of the total production cost of the products. Thus, the way to produce energy can play a significant role decreasing operational expenditures. Indeed, the best option to reduce the energy related-cost was the HRES involving biogas cogeneration plus electricity using PV-systems. The production cost was decreased using this alternative 5.6% compared to the option without HRES (i.e., electricity from grid and heat from boiler using natural gas). The CapEx of introducing HRES systems is higher than conventional pathways. Nevertheless, this increase was not significative on the economic performance of the process. The environmental assessment demonstrated the lower carbon footprint of the biorefinery when introducing HRES instead of common energy supply methods. The carbon footprint was decrease about 15%, while the water footprint was not affected in a high proportion.

As conclusion, biorefineries are complex systems where fossil fuels still are used to supply a share of the heat and power demand by producing renewable energy using renewables such as sunlight and biomass. Hybrid Renewable Energy Systems (HRES) are potential strategies to reduce the use of fossil fuels and decrease the existing dependence on non-renewable sources. Energy supply is a mandatory topic to be analyzed together biorefineries since not only productive schemes must be assessed. AV was the best raw material to produce levulinic acid and derivatives since this raw material has a high C_6-sugars content. Nevertheless, the levulinic acid yield obtained at lab-scale can be improved by increasing the reaction time and acid concentration. CPH is a potential raw material to be used for biorefining but other products must be assessed. Even, pretreatment strategies must be assessment to remove lignin and other components.

Keywords: *Hybrid renewable energy systems, waste to energy, biorefineries, energy transition, decarbonization, and techno-economic and environmental analysis.*

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