

Life Cycle Analysis of Biotechnological Processes based on the Composition of the Raw Material. Eucalyptus, Avocado, and Plantain cases in a Biorefinery System

Jhonny A. Poveda-Giraldo, Sara Piedrahita-Rodríguez, Carlos A. Cardona-Alzate*

Institute of Biotechnology and Agribusiness, Departamento de Ingeniería Química, Universidad Nacional de Colombia, Manizales, Caldas, 170003, Colombia.

ccardonaal@unal.edu.co

Agricultural and forest crops are characterized by the production of a high amount of residues during their processing. The disposal of this biomass can mitigate the environmental impact through its integral use in the biorefinery context. In this work, the processing of Eucalyptus spp. chips, avocado seed and, plantain pseudostem distributed in five biorefineries scenarios were analyzed. The best three schemes were chosen based on chemical composition and their potential to obtain products as phenolic compounds considering a robust economic allocation. These three biorefinery configurations were assessed in economic and environmental terms. The Life Cycle Analysis (LCA) methodology was used to determine the environmental impacts associated. As a main economic result, all scenarios did not present economic viability for the selected processing scale, with losses higher than 3.3 M USD/y. From the environmental perspective, the significant steam demand influenced the different impact categories. However, the food waste-based biorefinery showed less environmental impact. This scheme presented positive impacts on wastewater treatment; the fertilizer concentration stage prevents the production of high amounts of liquid streams to be generated in the process.

1. Introduction

During the wood production process, forest crops generate large amounts of residues. In Colombia, there is about 23 wt% of residues generated in such practices (Poveda, 2019). Likewise, other types of crops also generate many residues almost on the same scale as forest crops, especially in tropical countries with high biodiversity. An example is the plantain and avocado crops that are highly demanded fruits both nationally and internationally. About 25 t of plantain pseudostem is generated in this crop for every 1,000 plantain fruits (Schieber et al., 2001). Another example is the avocado, where 18 % of the fruit corresponds to residues whereby the seed is 20 % (Ahmed et al., 2012). The use of these types of biomass becomes interesting to obtain value-added products through biorefinery schemes, mitigating the adverse environmental effects caused by the disposing methods. To reach this purpose successfully, biorefinery systems must be designed according to the amount of raw material available to be transformed. However, in a single region, it is difficult to find the scales required to make the process profitable. Currently, alternative solutions to this problem require to develop the concept of integration of raw materials in biorefineries. This concept is promising in solving the scale requirement problem and may even help improving process efficiencies. The effects caused to the environment after these integrations have not been extensively studied. It is common to focus the research only on the use of one raw material and with flow rates greater than the real capacity of a study region. Previous works have found a better economic feasibility and environmental impact of a plantain peel based biorefinery to produce biogas, ethanol, xylitol, and syngas compared with a stand-alone process of biogas production (Parra et al., 2019). Aristizábal et al (2020) demonstrated that a coffee waste biorefinery presents an economic pre-feasibility at higher scales compared to a stand-alone process for the production of furfural and biogas, and it is environmentally unfriendly because of the extensive use of reagents and utilities. The environmental assessment of processes is used to determine the sustainability of obtaining some products from raw materials. This assessment allows decisions about what could be improved within the process. For the environmental

assessment of systems such as biorefineries, the LCA is considered as a robust methodology since it estimates the environmental impact of a process or system throughout the total life cycle, from a determined scope and an adequate interpretation (Finnveden et al., 2009). The LCA is currently considered reliable and useful (Tarighaleslami et al., 2019). Environmental assessment through LCA methodology of biorefineries with raw material integration has been poorly studied. This work aims to evaluate the environmental impacts associated with food waste and wood-based biorefineries. This evaluation was developed using the LCA methodology, analyzing the process based on the elemental and combined composition of the raw materials. Five scenarios were proposed as follows: scenario 1 (Sc.1) corresponds to the biorefinery based on Eucalyptus; scenario 2 (Sc.2) is based on the integration of Eucalyptus and plantain pseudostem; scenario 3 (Sc.3) relates to the integration of Eucalyptus with avocado seed; scenario 4 (Sc.4) consists of the integration of the three feedstocks; finally, scenario 5 (Sc.5) corresponds to the integration of plantain pseudostem and avocado seed.

2. Methodology

2.1 Selection of scenarios

Based on the composition of the raw materials, the most relevant schemes to obtain a representative environmental comparison between them were evaluated. The products (ethanol, vanillin and vanillic acid) of the base-case biorefinery (Sc.1), without raw materials integration, were fixed to be obtained in the other scenarios using Eucalyptus. Sc.2, 3 and 4 have the same products as the base-case, and Sc.5 was proposed to obtain oil, biogas, digestate, and ethanol. Sc.1 and Sc.5 were selected to carry out the complete analysis in this work. Sc.2, 3, and 4 were analyzed to define the best integration configuration at the desired scale. Table 1 shows the chemical composition of each raw material. The content of cellulose and lignin is highlighted as the most relevant parameter. In the case of Sc.2, in which Eucalyptus is integrated with plantain pseudostem, an increase in the amount of cellulose of the "global raw material" is noted, improving the production of ethanol, even with a low integration ratio. In Sc.3, in which the integration involves the Eucalyptus and the avocado seed, the low cellulose and lignin content of the avocado seed would cause a very high feedstock ratio to justify the integration. In other words, the proportion of avocado seed must be considerably more significant than the Eucalyptus, which can be a problem in terms of raw material acquisition. Finally, Sc.4, an improvement in the cellulose and lignin global content could be expected with adequate integration ratios according to the availability of feedstocks. The low lignin content of avocado seed and plantain pseudostem can benefit the availability of cellulose to be processed (for ethanol production), and in the case of phenolic compounds, Eucalyptus will be able to meet these requirements due to its abundant lignin content. Analyzing these scenarios in terms of composition, Sc.4 was selected as a complete integrated biorefinery to compare with Sc.1 and Sc.5. Scenarios 2 and 3 were finally discarded for further analysis.

Table 1: Chemical composition of raw materials (wt%)

Component	Avocado seed (Bora et al., 2001)	Plantain pseudostem (Daza et al., 2016)	Eucalyptus spp. Chips (Poveda, 2019)
Moisture	11.26	50.36	4.72
Cellulose	8.52	20.15	40.67
Hemicellulose	38.37	9.34	18.70
Lignin	4.72	6.88	36.58
Extractives	33.10	9.34	3.50
Lipids	1.79	N.R.	N.R.
Ash	2.26	3.93	0.55

N.R: Not Reported

2.2 Process simulation

Three biorefinery scenarios (Sc.1, 4 and 5) were proposed and designed based on the scale of raw material available in the northwest regions (Córdoba and Montes de María) in Colombia. Sc.1 involves the production of ethanol and phenolic compounds such as vanillin and vanillic acid, considering a feedstock of 13 t/d of Eucalyptus spp. chips (large scale). Sc.4 regards 17.4 t/d of a mixture of Eucalyptus spp. chips, avocado seed (*Persea americana* Mill. cv. Lorena), and plantain pseudostem (*Musa paradisiaca*). Sc.5 produces oil, biogas, digestate, and ethanol from 4.4 t/d of a mixture of avocado seed and plantain pseudostem (small scale). All scenarios were simulated in the software of Aspen Plus v9.0 (Aspen Technology, Inc., USA) using experimental data reported in the literature. The thermodynamic method of Non-Random Two-Liquids (NRTL) coupled with the equation of state of Hayden O'Connell was selected to calculate the activity coefficients of the components in the liquid and gas phases.

2.3 Process description

2.3.1 Scenarios 1 and 4

Raw materials were dried (until a moisture content below 10 %) and ground. Then, the feedstocks were pretreated with a solution of NaOH 8 % in a solid-to-liquid ratio of 1:5 (w/v) at 130 °C (Poveda, 2019). After pretreatment, both fractions were separated by filtration. Liquid fraction (black liquor) was concentrated to 60 g/L and oxidized with air in a pressurized reactor (10 bar) at 120 °C. Phenolic compounds were separated and purified in five main steps at 25 °C (Poveda, 2019). i) Ultrafiltration membrane was selective to lignin. ii) Adsorption column packed with a non-polar resin to separate vanillin from vanillic acid. iii) Absorption column with benzene as a solvent to separate each phenolic compound from water. iv) Distillation to recover the solvent. v) Crystallization at 2 °C to purified phenolic compounds. The solid fraction after alkali pretreatment (rich in hexoses and pentoses) was used to produce ethanol. Firstly, this solid stream was pretreated with dilute sulfuric acid (5 vol %) (Carrasco and Roy, 1992). Then, the cellulose-rich solid was separated by filtration and hydrolyzed with enzymes at 50 °C in a mass ratio between solid and enzyme of 10:1.5 (Aristizábal, 2015). Afterward, glucose liquor was concentrated to 40 g/L and fermented at 32 °C with *Saccharomyces cerevisiae* (Moncada et al., 2016). Finally, ethanol was separated by distillation columns and purified by adsorption column packed with molecular sieves. Figure 1a summarizes the processing methodology for Sc.1 and 4.

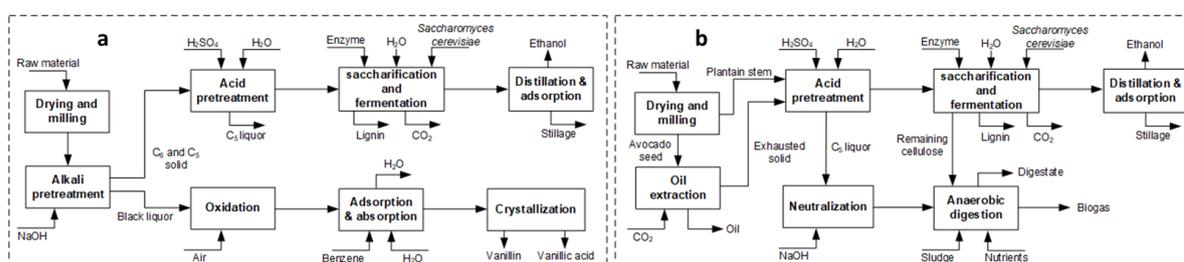


Figure 1: Process block diagram of (a) Sc.1, (b) Sc.4 and 5.

2.3.2 Scenario 5

The avocado seed was dried and grounded. Then, it was submitted to supercritical CO₂ extraction technology, using a mass ratio of 5:1 (CO₂:dry raw material). The main fatty acid that is present in the avocado seed is linoleic acid (38.9 % of the total fatty acids) (Bora et al., 2001). The conditions of this process were taken from Moncada et al., (2014). Then, the non-oil stream was mixed with the stream of plantain pseudostem that was previously conditioned (Figure 1b). The integrated stream was pretreated with dilute sulfuric acid, hydrolyzed with enzymes and fermented at the same conditions of Sc.1 and 4. The C₅ liquor-rich stream obtained in the dilute sulfuric acid pretreatment was neutralized and then sent to an anaerobic digestion process for obtaining biogas and digestate. Buswell model was used, to generate biogas (CH₄ and CO₂) (Bacherizo et al., 2016).

2.4 Economic assessment

The economic assessment was performed considering the mass and energy balances of the biorefineries. Equipment sizing and capital cost were estimated through the software of Aspen Process Economic Analyzer (Aspen Technology, Inc., USA). Production cost was considered as the sum of raw material, reagents, utilities (low and medium pressure steam, cooling water, and electricity), and capital cost (Poveda, 2019). Raw materials cost was calculated as the transport cost for a freight vehicle (5 t approximately) that travels a distance between the crop or food processing to the location of the biorefineries. Reagents and utilities cost, as well as product prices, were taken from the literature (Poveda, 2019). The investment cost annualization was performed by calculating the equivalent annual cost (Poveda, 2019). Likewise, the economic assessment considers a project lifetime of 10 y and economic indexes of the Colombian regions, such an annual interest rate of 25 %.

2.5 Environmental assessment

The environmental assessment was performed through the LCA methodology considering only the process stage. The gate-to-gate approach was proposed to assess the impacts of the reagents, utilities generation, raw material processing, and their emissions. The emissions of the transport of the feedstock were considered in the LCA, which includes a 5 t freight truck and distances of 37, 159, and 37.4 km between the regions of Córdoba, and Montes de María (in the north of Colombia), to the biorefinery. The software SimaPro v8.3 (Pre-Consultants 2016, Netherlands) and the EcoInvent database were used to measure the environmental impact. The assessment was performed using the ReCiPe Midpoint (H-hierarchist version) as the characterization

method and 1 kg of ethanol as the functional unit. The mass and energy balances of the biorefinery scenarios were considered as input data of the process. The environmental analysis through the LCA was quantified through 8 impact categories: climate change (CC), terrestrial acidification (TA), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), freshwater ecotoxicity (FE), agricultural land occupation (ALO), water depletion (WD) and fossil depletion (FD).

3. Results and discussion

3.1 Techno-economic assessment

The ethanol productivities for Sc.1, 4 and, 5 were 16.4, 19.4, and 7 kg/h. The productivity for vanillic acid was 1.54 kg/h for Sc.1 and 1.64 kg/h for Sc.4. In the case of vanillin, Sc.1 produced 2.87 kg/h and Sc.4 4.32 kg/h. Sc.5 reached oil, biogas, and digestate productivity of 0.13 kg/h, 3.14 kg/h, and 18 t/h. Sc.4 improves biorefinery production, being the right integration of raw materials to reach the objective. Likewise, an improvement in the productivity of phenolic products is also noted. Although Sc.5 have different product configuration, it is possible to obtain diverse value-added products due to the composition of the feedstock, such as the avocado seed oil. Finally, the selection of the products of a biorefinery is governed by the potential that the feedstocks have to be transformed, given its composition. The integration of feedstocks can be an interesting pathway to improve productivity. The yields obtained from ethanol for the three scenarios were 0.03, 0.027, and 0.042 kg/kg total raw material for Sc.1, 4, and 5. The integration rate defined for Sc.4 makes the yield similar to that obtained by Sc.1. This result awakens the need to evaluate different integration rates when the objective is to improve these values. The high ethanol yield of Sc.5 is explained by the total lignin content present in the integration is lower than that obtained for Sc.1 and 4, easing the accessibility of the cellulose. From the economic view, Sc.1 and 4 were mainly affected by capital investment. This cost was determined as the direct cost of the equipment in each scenario, having values of 1.94 and 2.08 M USD/y. These costs are remarkably low compared to those reported by Solarte et al. (2018), due to the scale managed and the availability of raw materials. As expected, the capital investment of Sc.4 is higher than Sc.1 since there are increased costs related with raw materials, reagents, and utilities. Sc.5 had a strong influence on the cost of utilities required (23.24 M USD/y). All three scenarios presented a negative profit margin, around 3.3 M USD/y for Sc.1 and 4, and 16.2 M USD/y for Sc.5. An alternative to improve this aspect is to consider more regions to increase the feedstock flowrates since the production cost would decrease (Serna et al., 2018), or produce more valuable products from the cellulose fraction (Cardona et al., 2018). This feasibility can be observed by calculating the Net Present Value (NPV).

3.2 Environmental analysis

Figure 2a-b illustrates the environmental impact of Sc.1 and Sc.4 through the LCA methodology. Both scenarios have similarities in the performance of the categories, where steam is the main contributor to the environmental impacts with the participation of 50-70 % in Sc.1 and 40-60 % in Sc.4, except in ALO and WD for both scenarios. These results are similar to those presented by Aristizábal et al. (2020). A high energy requirement of steam induces a high volume of water in boilers, affecting the water resources and overall biodiversity of the region. Besides, the proposed boiler uses coal mixed with small amounts of oil as fuel, harming the environment after burning due to the generation of greenhouse gases (GHG) emissions, such as CO, CO₂, SO_x and, NO_x compounds. A reaction of these released gases to the air could take place with water from the atmosphere and produce sulfur and nitrogen-based acids precipitating as acid rain. Fossil fuel burning affects the decrease of non-renewable resources (FD) and allows the formation of small particles (PMF) according to the dirtiness. After fuel combustion, GHG's have a negative environmental impact; their inhalation is harmful to human health (HT) and/or the generation of particulate matter alters the soil ecosystem. These gases negatively affect global warming (CC) through smog generation (PCO). The possible formation of acid rain would affect the people (HT) and the ecosystem (TA and FE) due to the increase of acidity in the environment. Followed by steam, NaOH is the second contributor to the environmental impact, ranging between 11–30 % for Sc.1 and Sc.4, as shown in Figure 2a-b. The extensive use of NaOH in alkali pretreatment, the alkaline output streams combined with water steam (e.g. evaporation), and the industrial NaOH production (chloralkali process), are the main reasons of the environmental impact. On the other hand, the high consumption of water as a reagent in dilutions (alkali and acid pretreatments, substrate-to-enzyme ratios for glucose production, and the water requirement for vanillin desorption), cause a high environmental impact in WD index (86 % for Sc.1 and 56 % for Sc.4), as shown in Figure 2a-b. Concerning solvent use, benzene has a share of less than 8 % for Sc1 and 4 % for Sc.4, mainly due to the industrial production by cracking or reforming of oil (Gentry, 2007). Likewise, benzene is a highly toxic solvent producing drowsiness, dizziness, and tachycardia at low concentrations. Figure 2 shows negative values (positive impact) of wastewater in WD since the wastewater treatment plant that was assumed in the biorefinery design. It would be possible to observe a similar positive environmental impact if specific treatments were performed on the gaseous and solid waste streams. Other alternative is to the implementation of additional

stages in the biorefinery scenarios to recover reagents in the output streams. Parra et al. (2019) showed that considering an acid pretreatment stage before anaerobic digestion negatively affects the environmental impact of the process. Also, the total environmental impact of the process was negative due to the acidified waste streams and the non-valorization of digestate.

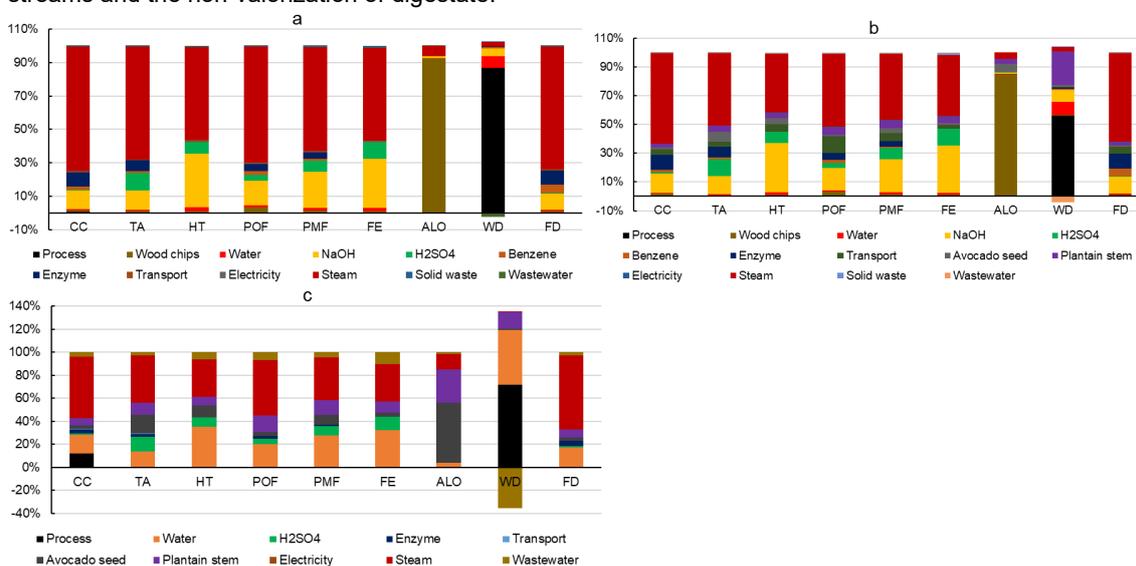


Figure 2: Environmental impact of (a) Sc.1, (b) Sc.4 and (c) Sc.5.

This is explained by the increase of raw material processing, demanding more amounts of reagents and utilities, and the increase of an extra trip for the acquisition of avocado seeds and plantain pseudostem in the areas of Montes de María. Figure 2c indicates the environmental impact of the food waste-based (Sc.5) biorefinery. As can be seen steam continues to strongly influence the impact categories of CC, TA, HT, POF, PMF, FE y FD with smaller shares (30-50 %) than Sc.1 and Sc.4. Similar to the other biorefinery schemes, the gases resulting from the fuel combustion in boilers affect the categories of CC, HT, PMF, and FD. The CO₂ emitted in the oil extraction stage must be considered, since this compound was not recirculated and instead was released into the environment. An increase in CO₂ in the atmosphere is responsible for the warming and acidification of the ocean (Connell et al., 2013). CO₂ is dissolved in water, which reacts and dissociates into a bicarbonate ion (HCO₃⁻) and a hydrogen ion (H⁺). The addition of more CO₂ from the atmosphere increases the amount of H⁺ contributing to the reduction of pH in the water sources, especially the ocean. On the other hand, biotechnological processes are characterized by the extensive use of water for their different process stages. The performance of the anaerobic digestion requires a quantity of water greater than 90 wt% (VDI, 2006), added to the high moisture content of the inoculum. In Figure 2c the wastewater is -35 %, explained by the low amount of liquid streams for treatment due to the valorization of the digestate as fertilizer. This by-product actively improves the environmental impact of a biorefinery because a non-disposal system as well as it would replace the use of fertilizers of petrochemical nature. By comparing the environmental impacts between all scenarios, Sc.5 is the most eco-friendly due to its low impact in all the categories, except in WD. For example, in climate change contributes to 52.9 kg CO₂-eq and human toxicity to 12.4 kg 1,4-DB-eq. This is explained due to the less raw material flowrate and avoids both black liquor oxidation and phenolic compound purification stages, which demand a high amount of energy.

4. Conclusions

The high availability and lignocellulosic content of agroindustrial waste in Colombia allow a potential use for the production of biochemical and bioenergy products (multiproduct portfolio) in a biorefinery perspective. The initial chemical composition is a crucial factor in the conceptual design of the processing schemes. A large scales raw material, (e.g. forest type), behaves as an essential source for generating products with a high market value when it is integrated with other smaller-scale biomass. By integrating food waste with a wood-based biorefinery, the economic viability increases due to a higher processing flow. The environmental impact is disadvantaged due to the increase in scale and its different chemical and energy requirements. High demand for steam affects the environmental impact due to previous processes to obtain it, such as the burning of fuel that generates GHG's, depletion and contamination of water sources, and toxicity due to the ingestion of harmful gases.

Acknowledgements

The authors thank to "Programa De Investigación Reconstrucción Del Tejido Social En Zonas De Posconflicto En Colombia" SIGP Code: 57579 with the investigation project "Competencias empresariales y de innovación para el desarrollo económico y la inclusión productiva de las regiones afectadas por el conflicto colombiano"; SIGP code: 58907, financed in the Colombia Scientific announcement (Contract NoFP44842-213-2018).

References

- Ahmed J., Lobo M.G., Ozadali F. 2012, Tropical and Subtropical Fruits. Postharvest Physiology, Processing and Packaging, Stewart Postharvest Review, John Wiley & Sons, Inc. Hoboken, New Jersey. US.
- Aristizábal-Marulanda V., Poveda-Giraldo J.A., Cardona Alzate C.A., 2020, Comparison of furfural and biogas production using pentoses as platform, *Science of the Total Environment*, 728, 138841.
- Aristizábal-Marulanda V., 2015, Jet biofuel production from agroindustrial wastes through furfural platform. M.Sc. Thesis, Universidad Nacional de Colombia, Manizales, Colombia.
- Baquerizo C.R.J., Pagés D.J., Pereda R.I., 2016, El modelo de Buswell. Aplicación y comparación. Principales factores que influyen en su aplicación, *Revista Virtual Pro. Spanish Language*, 168, 1–23.
- Bora P.S., Narain N., Rocha R.V.M., Queiroz Paulo M., 2001, Characterization of the oils from the pulp and seeds of avocado (cultivar: Fuerte) fruits, *Grasas y Aceites*, 52(3–4), 171–174.
- Cardona Alzate C.A., Solarte Toro J.C., Gómez Á., 2018, Fermentation, thermochemical and catalytic processes in the transformation of biomass through efficient biorefineries, *Catalysis Today*, 302, 61–72.
- Carrasco F., Roy C., 1992, Kinetic study of dilute-acid prehydrolysis of xylan-containing biomass, *Wood Science and Technology*, 26(3), 189–208.
- Connell S.D., Kroeker K.J., Fabricius K.E., Kline D.I., Russell B.D., 2013, The other ocean acidification problem: CO₂ as a resource among competitors for ecosystem dominance, *Philosophical Transactions of the Royal Society B: Biological Sciences*, 368(1627), 1–9.
- Daza Serna L.V., Solarte Toro J.C., Serna Loaiza S., Chacón Perez Y., Cardona Alzate C.A., 2016, Agricultural waste management through energy producing biorefineries: The Colombian case, *Waste and Biomass Valorization*, 7(4), 789–798.
- Finnveden G., Hauschild M.Z., Ekvall T., Guinée J., Heijungs R., Hellweg S., Koehler A., Pennington D., Suh S., 2009, Recent developments in Life Cycle Assessment, *Environmental Management*, 91(1), 1–21.
- Gentry J., 2007, Benzene production and economics: A review, *Asia-Pacific Chemical Engineering*, 2, 272–277.
- Moncada J., Cardona C.A., Higueta J.C., Vélez J.J., López-Suarez F.E., 2016, Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments, *Chemical Engineering Science*, 140, 309–318.
- Moncada J., Tamayo J.A., Cardona C.A., 2014, Techno-economic and environmental assessment of essential oil extraction from Citronella (*Cymbopogon winteriana*) and Lemongrass (*Cymbopogon citratus*): A Colombian case to evaluate different extraction technologies, *Industrial Crops and Products*, 54, 175–184.
- Parra D., Solarte J.C., Cardona C.A., 2020, Techno-economic and environmental analysis of biogas production from plantain pseudostem waste in Colombia, *Waste and Biomass Valorization*, 11, 3161–3171.
- Poveda G.J.A., 2019, Biorefineries based on catalytic conversion of biomass for the production of phenolic compounds from *Eucalyptus grandis* and *Calendula officinalis* residues, M.Sc. Thesis, Universidad Nacional de Colombia, Manizales, Colombia.
- Ramírez D.P., Marulanda V.A., Aroca G., Quintero J., Martínez A., Cardona C.A., 2017, Analysis of the ethanol and butanol production at different scales from plantain peel and *Eucalyptus globulus*, 5th International Conference on Sustainable Solid Waste Management, 1–9.
- Schieber A., Stintzing F.C., Carle R., 2001, By-products of plant food processing as a source of functional compounds - recent developments, *Trends in Food Science & Technology*, 12, 401–413.
- Serna-Loaiza S., García-Velásquez C.A., Cardona C.A., 2018, Strategy for the selection of the minimum processing scale for the economic feasibility of biorefineries, *Biofuels, Bioproducts and Biorefining*, 1–13.
- Solarte-Toro J.C., Romero-García J.M., López-Linares J.C., Ramos E.R., Castro E., Cardona C.A., 2018, Simulation approach through the biorefinery concept of the antioxidants, lignin and ethanol production using olive leaves as raw material, *Chemical Engineering Transactions*, 70, 925–930.
- Tarighaleslami A.H., Kambadur S., Neale J.R., Atkins M.J., Walmsley M.R.W., 2019, Sustainable energy transition toward renewable energies in the New Zealand dairy industry: An environmental life cycle assessment, *Chemical Engineering Transactions*, 76, 97–102.
- Verein Deutscher Ingenieure (VDI), 2006, Fermentation of organic materials. Characterization of the substrate, sampling, collection of material data, fermentation test, VDI 4630. Düsseldorf, Germany.