

Article

Equation-Oriented Modeling and Optimization of a Biorefinery Based on Avocado Waste

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Abstract: Due to the growth in the consumption of avocado in recent years, the amount of waste caused by avocado peel and seed has increased. Avocado waste can be transformed into valuable products such as energy, biofuels, and biological products using integrated processes in a biorefinery. This paper considers the detailed modeling, simulation, and optimization of a biorefinery for the production of phenolic compounds, bioethanol, biological xylitol, syngas, and electrical power from avocado seed and peel, using Aspen Plus in equation-oriented mode as a process simulation tool. For a biorefinery in nominal conditions, it is possible to achieve a gross profit of approximately 30×10^6 USD/year for capital costs of USD 31.4×10^6 , while the combined effect of process optimization and heat integration allows reaching a gross profit of 37×10^6 USD/year for capital costs of USD 30.7×10^6 . These results of the optimized plant show its potential to take advantage of avocado seed and peel in a profitable and sustainable way. This detailed equation-based model paves the way for superstructure optimization of a biorefinery for avocado waste processing.

Keywords: biorefinery; avocado waste; process modeling; process optimization; process integration



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1. Introduction

The consumption of avocado and its derivatives has grown significantly in the past few years, from 3.3 million tonnes in 2008 to 8.7 million tonnes in 2021 [1]. The growth of avocado production driven by this increased consumption has resulted in large amounts of waste, namely, avocado peel and seed, which can amount to 42% of the fruit weight [2]. Currently, most of this waste is discarded and underutilized, but the disposal of this waste may imply significant costs, environmental risks, and health concerns [3]. This avocado waste could be valorized and converted into valuable co-products via the implementation of biorefineries. The processing of avocado waste using integrated processes in a biorefinery context rather than single processes would help move towards a circular bioeconomy with zero waste. Such biorefineries would allow obtaining energy, fuels, and biological products in a synergetic way in a single plant by taking advantage of the heating value and chemical composition of avocado waste, which is mainly composed of lignocellulosic material. As a source of bioenergy and biofuels, which prevent the use of fossil resources, avocado waste has the advantage of not competing with food production, in comparison with other renewable sources [4]. Biofuels can be produced from avocado in several forms: as biogas via biochemical conversion [5]; as syngas via gasification [6]; as biodiesel via the

transesterification of triglycerides [7]; as biooil via pyrolysis and liquefaction [8]; as biochar via pyrolysis [9]; and as bioethanol via fermentation [10]. Other valuable chemicals, such as bio-based xylitol, can also be obtained via fermentation [11], and these fermentation products are particularly interesting since avocado waste contains a high fraction of sugars, such as glucose and xylose, in polymeric form [12]. Fermentation can be preceded by several pretreatment steps, including enzymatic hydrolysis [13], and can be performed by a single microorganism or by two microorganisms that are able to simultaneously ferment pentoses and hexoses [14]. Several co-products, including starch, proteins, avocado seed oil, natural dyes and colorants, and natural antioxidants such as phenolic compounds, can also be recovered from avocado waste. Starch is particularly abundant in avocado seeds and can be used for the food and textile industries [3], while phenolic compounds are particularly relevant, owing to the significant phenolic content and antioxidant activity of avocado peel and seed and the importance of phenolic compounds for the food industry and medicinal applications [15,16]. Other bioactive compounds with pharmaceutical applications, such as anti-inflammatory and antimicrobial activity, may also be obtained from avocado waste, and appropriate processing can transform avocado waste into biopolymers and biomaterials [13]. Solvent extraction and supercritical CO₂ extraction have been suggested as the methodologies with the highest efficiency for the extraction of phenolic compounds [17,18]. The remaining exhausted solids are composed of polysaccharides that can still be appropriately processed to obtain bioenergy, biofuels, biochemicals, and biomaterials as mentioned.

However, before the concept of a biorefinery based on avocado waste can be fully implemented in practice, detailed modeling, simulation, and optimization studies, techno-economic analysis, and life cycle assessment must be performed. This is crucial to improve the yield, efficiency, profitability, and environmental sustainability of such processes. To this end, mass and energy integration is essential to minimize raw materials and energy consumption, economic costs, and environmental impact. This process integration and the simultaneous production of several products in the biorefinery may even be the only way to ensure a profitable and sustainable plant. Also, the successful implementation of a biorefinery based on avocado waste must involve a combination of the most appropriate physical, chemical, and biological steps in a proper order to enhance the process efficiency. For this purpose, several process alternatives may need to be evaluated and compared, which will greatly benefit from the use of modeling and simulation tools.

In this context, Dávila et al. [19] investigated the modeling and simulation of a biorefinery for avocado processing. This biorefinery is designed to produce microencapsulated phenolic compounds, oil, xylitol, ethanol, syngas, and electrical power, by taking advantage of the oil from avocado pulp and the lignocellulosic material from avocado seed and peel. For this purpose, the biorefinery includes a phenolic compounds extraction unit using supercritical fluid extraction, an oil extraction unit, a sugar plant, a xylitol plant using xylose fermentation, an ethanol plant using glucose fermentation, and a cogeneration plant. It is shown that mass and energy integration and complete utilization of the avocado fruit according to a biorefinery concept are essential to ensure process profitability and to reduce the environmental impact. Restrepo-Serna et al. [20] reinforced this idea by showing that integral biorefineries lead to profit margins of 47.41% and 43.05% for avocado seed and peel, respectively, compared to profit margins of 21.40% and 21.14% of standalone processes for avocado seed and peel, respectively. In contrast to the study by Dávila et al. [19], it also takes advantage of the starch that is present in avocado seed to produce ethanol and proposes combined glucose and xylose fermentation to form ethanol from avocado peel. Piedrahita-Rodríguez et al. [21] considered a techno-economic analysis of a biorefinery for the production of biogas, avocado seed oil, and bioethanol using plantain and avocado waste as raw material. Based on experimental results for the production of biogas and avocado seed oil, it was shown that the proposed biorefinery with a 1:5 avocado to plantain ratio allows achieving a positive net present value in less than 2 years of project lifetime. In addition, Solarte-Toro et al. [22] performed environmental life cycle assessment and

social impact assessment of two biorefineries, one for the production of avocado oil and animal feed and the other for the production of guacamole. It was concluded that guacamole production has the best environmental performance but the worst economic and social results, while the environmental performance of avocado oil production is improved if the animal feed production line is excluded.

This paper focuses on the detailed modeling, simulation, and optimization of a biorefinery for the production of phenolic compounds, bioethanol, biological xylitol, syngas, and electrical power from avocado peel and seed, based on the elementary models of a process simulation tool, namely, Aspen Plus. The process that is described in this paper is, in many ways, similar to the one proposed by Dávila et al. [19], which is the benchmark and starting point for this modeling and optimization study. However, the current paper introduces a novelty with respect to previous studies by describing in detail all the process specifications, by using an equation-oriented framework, and by optimizing the operating conditions via process optimization and heat integration. This, in turn, will allow researchers and practitioners in this field to fully implement the entire biorefinery model in an equation-oriented framework, to reproduce the optimal conditions and results of this study, and to test methodologies for process integration and optimization.

2. Process Description

Aspen Plus v12.1 in equation-oriented mode was used for process simulation. The process specifications and constraints described in this section were implemented in two ways: either (i) by choosing the appropriate specifications for the blocks and inlet streams in the process; or (ii) by using the “EO Configuration” options “Spec Groups” and “Connection” to specify changes to calculated, constant, and optimized variables and the relations between each one of these variables and the other variables. Appendix A provides more information about the configuration of the “Spec Groups” and “Connection” options and how this configuration results from the process description in this section. The “EO Configuration” option “Objective” was used to specify the objective function for process optimization. The database BIODFMS3 from the National Renewable Energy Laboratory, which contains lignocellulosic compounds (lignin, cellulose, and hemicellulose) that are not present in the original databases of Aspen Plus, was imported into Aspen Plus. The NRTL model was used. Aspen Process Economic Analyzer was used to calculate the capital and operating costs. In addition, Aspen Energy Analyzer was used to compute the targets for energy and cost savings owing to heat integration via pinch analysis. In this work, the heat exchanger network that achieves minimum energy requirements is not obtained explicitly, but the cost savings owing to heat integration are considered for the computation of the operating costs. Further application of energy integration to the process flowsheet would require the design of a network for minimum energy requirements and its implementation in the process flowsheet, which is considered out of the scope of this study.

The so-called NRTL model in Aspen Plus is a base method that includes several models, one for each thermodynamic property. In the case of the vapor phase properties, the NRTL model considers an ideal gas. Initially, the NRTL-HOC model in Aspen Plus, which considers the Hayden–O’Connell (HOC) model for vapor phase properties, was chosen since this model was used in the study by Dávila et al. [19]. However, the use of the NRTL-HOC model resulted in several errors and inconsistencies when it was combined with the presence of solids in the process flowsheet due to the lack of data required to use the HOC model. This led to a change to the NRTL model. Although the assumption of an ideal gas may cause some inaccuracies in the vapor phase at high pressures, the only part of the process with significantly high pressures is the supercritical extraction, where the corresponding fluids are supercritical fluids, which are modeled by Aspen Plus as liquids.

The process for the valorization of avocado waste biomass is designed to have the capacity to process the mass flow rate of avocado peel and seed that corresponds to 10 ton/h of avocado [19], considering the average values of the mass fraction of peel and seed equal to 11% and 17%, respectively [20], which means that it processes 1.1 ton/h of

avocado peel and 1.7 ton/h of avocado seed. According to Restrepo-Serna et al. [20], there exist at least three departments in Colombia (Antioquia, Caldas, and Tolima) where the avocado production of each one of these departments would allow supplying the required mass flow rate of avocado peel and seed for the proposed process. Hence, the required flow rate of avocado peel and seed can be provided without the need to mix these raw materials with other types of waste. The mass fractions of cellulose, hemicellulose, lignin, extractives, moisture, and ashes correspond to the ones reported by Dávila et al. [19] and are shown in Table 1. The extractives, which consist of high-value phenolic compounds with several benefits, are modeled as phenol, and the ashes are modeled as SiO_2 . The peel and seed fractions enter the extraction plant shown in Figure 1 at ambient temperature and atmospheric pressure and are subject to drying at 40 °C to decrease the moisture on a wet basis to 5.12% [19], using air at atmospheric pressure with the mass flow rate required to achieve 100% relative humidity in the air outlet stream. Then, the dry solids are fed to the extractor, which is modeled as a stoichiometric reactor and operated at 40 °C and 250 bar with supercritical CO_2 as the solvent and ethanol as the co-solvent, according to the conditions tested by Páramos et al. [18]. The conversion of extractives (modeled as phenol) in the solids to phenol in the fluid phase is such that an extraction yield of 5.6% with respect to the mass flow rate of solids is achieved [18]. As mentioned, the extractor in this process is modeled as a stoichiometric reactor that simply transfers a fraction of the phenolic compounds (modeled as phenol) in the solids inlet stream to the supercritical outlet stream. The fraction of phenolic compounds that is transferred to the supercritical phase, that is, the extraction yield, was determined by Páramos et al. [18] from actual experiments in certain conditions of temperature, pressure, and mass flow ratios of CO_2 to solids and ethanol to solids, not from the thermodynamic models. This means that it is only necessary to make the process conditions match the experimental conditions used by Páramos et al. [18] to ensure the validity of the extraction yield considered in the simulation. Hence, the thermodynamic model used to simulate the supercritical extraction is not relevant for this process. It is assumed that 10% of the CO_2 and ethanol is lost when the extractor is opened as mentioned by Dávila et al. [19], which is modeled by a separator with a split fraction of 0.1 for CO_2 and ethanol. The extractor outlet stream goes through a valve to reduce its pressure and is fed to a collection vessel at 50 bar [19]. The mass flow rate of CO_2 to the extractor corresponds to an initial volume of 50 cm^3 plus a flow rate of 2 cm^3/min for 30 min for 10 g of solids in the extractor and is computed from the density of CO_2 at 40 °C and 250 bar, which results in a mass flow ratio of 11.02 g of CO_2 per g of solids at the extractor inlet [18]. The CO_2 to the extractor is processed as follows: fresh CO_2 at ambient temperature and 50 bar, the pressure of the collection vessel, is mixed with a recycled CO_2 -rich stream to achieve the required mass flow rate of CO_2 to the extractor; the CO_2 stream is cooled down to −20 °C in a heat exchanger [19]; the pressure is increased to 250 bar, the pressure of the extractor, in a pump with an efficiency of 0.8; and the CO_2 stream is heated up to 40 °C, the temperature of the extractor. The mass flow rate of ethanol to the extractor corresponds to a mass flow ratio of 1.5 g of ethanol per g of solids at the extractor inlet [18]. The ethanol to the extractor is processed as follows: fresh ethanol at ambient temperature and atmospheric pressure is mixed with a recycled ethanol-rich stream to achieve the required mass flow rate of ethanol to the extractor; the pressure is increased to 250 bar, the pressure of the extractor, in a pump with an efficiency of 0.8; and the ethanol stream is heated up to 40 °C, the temperature of the extractor. The outlet stream of the collection vessel is fed to a heat exchanger, where it is heated up to 67.5 °C so that the mass recovery of CO_2 in the vapor is approximately equal to the mass recovery of ethanol in the liquid, and then to an adiabatic flash, where the vapor stream corresponds to the recycled CO_2 -rich stream, while the liquid stream proceeds to a filter. In this filter, the solids are fully separated with a liquid load of 10^{-7} in the solid outlet, and both the solid outlet and liquid outlet go through valves to reduce the pressure to 1 bar, which is the pressure at which the remaining process is operated [19]. The solid outlet stream is directed to a sugar plant, while the liquid outlet stream is processed as follows: it is cooled down to 14 °C in a

heat exchanger and is then fed to an adiabatic flash so that the mass recovery of CO₂ in the vapor is approximately equal to the mass recovery of ethanol in the liquid; the vapor outlet corresponds to a CO₂-rich stream that is not recycled due to its low pressure, while the liquid outlet is heated up to 80 °C in a heat exchanger and is then fed to an adiabatic flash so that the mass recovery of extractives in the liquid is almost complete and the mass recovery of ethanol in the vapor is as high as possible; and the liquid outlet corresponds to extractives dissolved in ethanol that can then be directed to a spray dryer and subject to the encapsulation of phenolic compounds, while the vapor outlet corresponds to the recycled ethanol-rich stream after condensation to a saturated liquid in a heat exchanger.

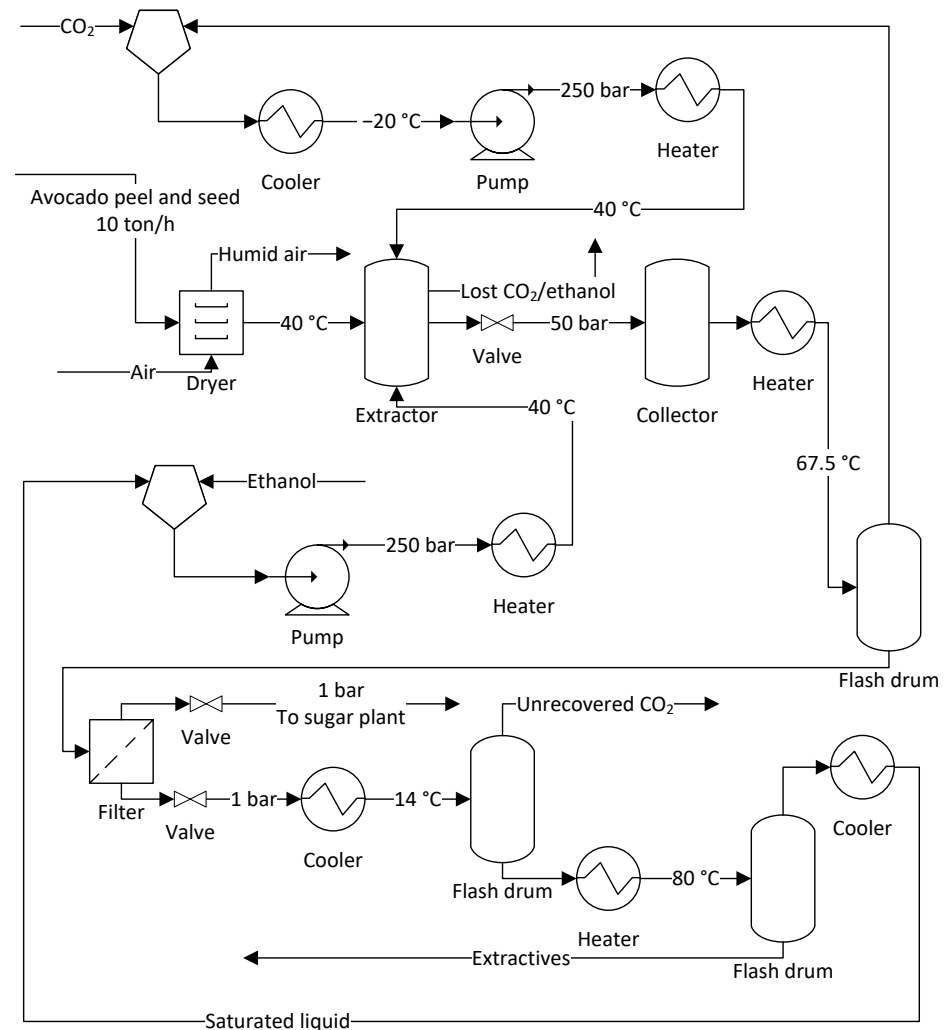


Figure 1. Schematic of the extraction plant.

Table 1. Mass fractions (in %) of cellulose, hemicellulose, lignin, extractives, moisture, and ashes in the avocado peel and seed.

Components	Peel	Seed
Moisture	7.33	7.02
Extractives	34.38	35.95
Cellulose	27.58	6.48
Hemicellulose	25.30	47.88
Lignin	4.37	1.79
Ashes	1.04	0.88

The process continues in the sugar plant shown in Figure 2 with the solid outlet of the filter at 1 bar. This solid stream is mixed with a liquid stream of 2% *w/w* H₂SO₄ in water at ambient temperature and atmospheric pressure for the acid hydrolysis of hemicellulose to xylose such that the mass flow rate of the diluted H₂SO₄ stream is 10 times the mass flow rate of solids in the solid stream [23]. The resulting mixture is heated up to 99 °C, just below the boiling point of water to prevent vaporization, in a heat exchanger. It is then fed to a stirred reactor for acid hydrolysis at 99 °C, where the residence time of 70 min and the reaction kinetics of the formation of xylose from hemicellulose correspond to the ones proposed by Aguilar et al. [23] for 2% *w/v* H₂SO₄ at 100 °C, which excludes the formation of furfural. The outlet stream of this reactor is cooled down to 50 °C in a heat exchanger [19] and is fed to a filter, where the solids are fully separated with a liquid load of 10^{-7} in the solid outlet. The solid stream corresponds to the initial solid stream without most of the hemicellulose, while the liquid stream contains an acid and aqueous solution of xylose. This liquid stream is processed as follows: it is fed to a valve, where the pressure is reduced to 0.3 bar, most of its water is evaporated in an evaporator with a vapor fraction of 0.5, and it is pressurized again to 1 bar by a pump with an efficiency of 0.8 [19]; the resulting liquid stream is cooled down to 25 °C in a heat exchanger; it is then mixed with 2% *w/v* NaOH in water at ambient temperature and atmospheric pressure in a neutralization reactor at 25 °C, where the mass flow rate of the NaOH solution is such that the pH at the outlet is increased to 6.5 since H₂SO₄ reacts with NaOH to form water and Na₂SO₄ [19]; and the outlet stream of this neutralization reactor, which corresponds to an aqueous solution of xylose with suspended Na₂SO₄, is directed to the xylitol plant. The solid stream is processed as follows: it is mixed with water at ambient temperature and atmospheric pressure to achieve a mass fraction of solids of 7% and heated up to 50 °C in a heat exchanger [19]; it is then fed to a stirred reactor for the enzymatic hydrolysis of cellulose to glucose at 50 °C, where the residence time of 6 h and the reaction kinetics of the formation of glucose from cellulose correspond to the ones mentioned by Khodaverdi et al. [24]; the outlet stream of this reactor is cooled down to 25 °C [19] and is fed to a filter, where the solids are fully separated with a liquid load of 10^{-7} in the solid outlet; and the solid stream corresponds to a lignin-rich solid stream without most of the initial hemicellulose and cellulose, which is directed to the cogeneration plant, while the liquid stream contains an aqueous solution of glucose, which is directed to the ethanol plant.

The xylitol plant in Figure 3 is fed with an aqueous solution of xylose with suspended Na₂SO₄. Its inlet stream is fed to a filter, where the solids are fully separated with a liquid load of 10^{-5} in the solid outlet. The solid stream corresponds to the Na₂SO₄ that was produced in the neutralization reactor, while the liquid stream contains an aqueous solution of xylose. This liquid stream is fed to a valve, where the pressure is reduced to 0.3 bar. Then, it is subject to evaporation in an evaporator, pressurized again to 1 bar by a pump with an efficiency of 0.8, and cooled down to 30 °C in a heat exchanger so that a concentration of 70 g L⁻¹ of xylose is reached and the conditions for the xylose fermenter are achieved [25]. Then, the stream is mixed with water at 30 °C and atmospheric pressure and fed to the xylose fermenter at 30 °C, where xylitol is formed and the conversion of xylose and water to xylitol and oxygen is such that a xylose productivity of 0.58 g L⁻¹ h⁻¹ in 96 h of fermentation is achieved for the liquid phase [25]. The mass flow rate of water is the one that is strictly needed for the required production of xylitol. Then, the resulting outlet stream is subject to evaporation in an evaporator and mixed with ethanol at ambient temperature and atmospheric pressure before entering a crystallizer at 40 °C [19] such that a mass fraction of 0.875 of ethanol in the water/ethanol solvent is achieved at the crystallizer inlet, and a solvent to xylitol/xylose mass ratio of 0.3 is achieved at the crystallizer outlet [26]. Then, the xylitol crystals can be recovered by filtration.

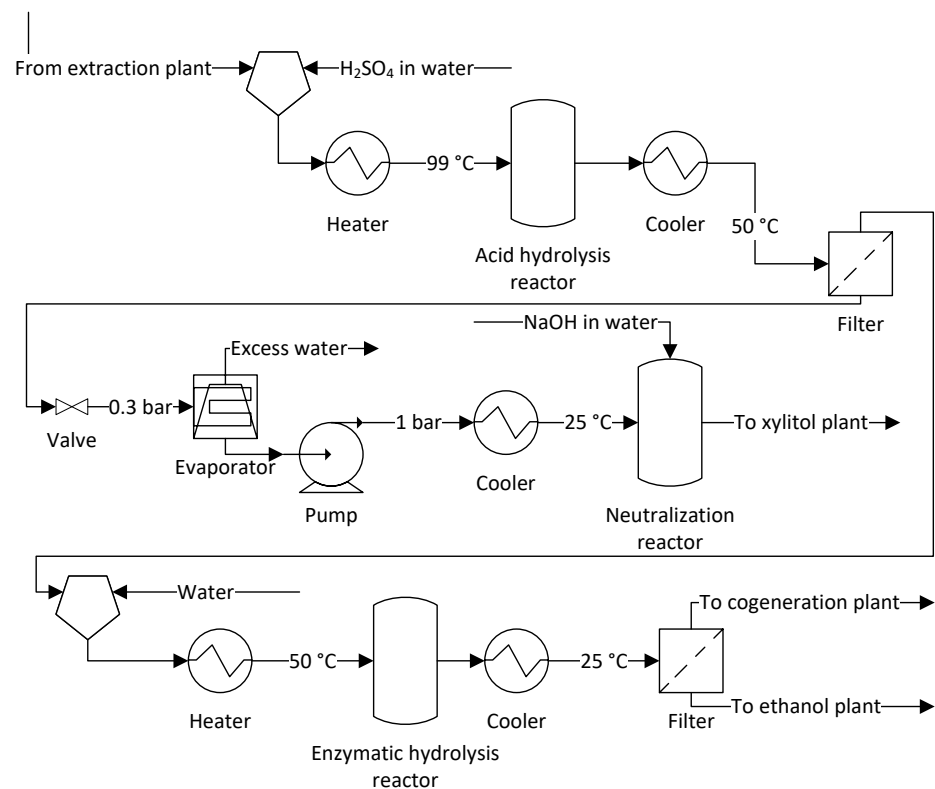


Figure 2. Schematic of the sugar plant.

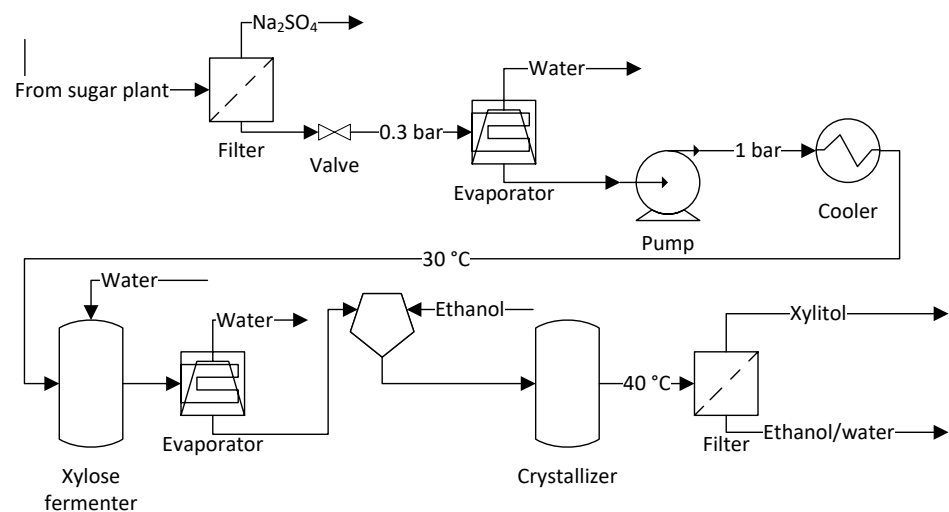


Figure 3. Schematic of the xylitol plant.

The ethanol plant in Figure 4 is fed with an aqueous solution of glucose. Firstly, its inlet stream is fed to a valve, where the pressure is reduced to 0.3 bar. Then, it is subject to evaporation in an evaporator, pressurized again to 1 bar by a pump with an efficiency of 0.8, and cooled down to 37°C in a heat exchanger so that a concentration of 51.29 g L^{-1} of glucose is reached and the conditions for the glucose fermenter are achieved [19]. The concentration of glucose is determined as the one that achieves an almost complete conversion of glucose and does not require increasing the fermenter volume. Then, the stream is mixed with a stream at 37°C and atmospheric pressure that contains a source of sufficient N and S for fermentation and fed to the glucose fermenter at 37°C , where ethanol is formed, the residence time is 20 h, and the reaction kinetics of formation of biomass and ethanol from glucose corresponds to the one mentioned by Rivera et al. [27]. The residence time is determined such that smaller residence times

decrease the ethanol yield, and larger residence times do not significantly increase the ethanol yield. The gas outlet stream is released from the fermenter, while the remaining outlet stream is fed to a filter, where the solids are fully separated with a liquid load of 10^{-7} in the solid outlet. The solid outlet is released from the process, while the liquid stream is a mixture of water, ethanol, unreacted glucose, and dissolved gases such as CO_2 , which is fed to two distillation columns in series, where the ethanol-rich product is fed from the liquid distillate of the first column to the second column and recovered from the vapor distillate of the second column, for which no liquid distillate is present. Its final composition is similar to the one of the water–ethanol azeotrope. The settings of these two columns are as follows: the distillate-to-feed ratio, the reflux ratio in the second column, and the mass fraction of vapor distillate in the first column are chosen to achieve a mass purity of ethanol of 0.5 in the liquid distillate of the first column and 0.91 in the vapor distillate of the second column, and a mass recovery of 99.5% of CO_2 in the vapor distillate of the first column and 99.99% of ethanol in the vapor distillate of the second column; the reflux ratio in the first column is 3; the number of equilibrium stages is 9 in the first column and 13 in the second column; and the feed stage is 3 in the first column and 8 in the second column. For both distillation columns in the ethanol plant, the reflux ratio was initially set to 3 to avoid large energy costs in the condensers and columns with a large diameter. Then, for the chosen reflux ratio, the number of stages and the feed stages were decided based on the temperature profile as a function of the stage number to eliminate excess stages, represented by several adjacent stages with constant temperature, while minimizing the flow rate of ethanol at the bottom. In the case of the second column, the reflux ratio was eventually adjusted along with the distillate-to-feed ratio to achieve a mass purity of ethanol of 0.91 in the vapor distillate and a mass recovery of 99.99% of ethanol in the vapor distillate. In both cases, the pressure in the column is 1 bar. The vapor distillate of the first column is fed to the bottom of an absorption column with three stages. At the top, an inlet stream of water at ambient temperature and atmospheric pressure is fed with a mass flow rate such that the mass recovery of ethanol at the bottom is 99.95%. The top outlet consists of a CO_2 -rich stream, while the bottom outlet is recycled to the feed stream of the first distillation column. Then, the resulting stream is heated up to 116 °C in a heat exchanger before entering molecular sieves, which are required to overcome the water–ethanol azeotrope. The molecular sieves are modeled via separators, where a split fraction of water of 0.001 in the product stream allows achieving the required purity of 99.95% of ethanol in that stream, which is then cooled down to 25 °C in a heat exchanger [19].

The cogeneration plant in Figure 5 is fed with a lignin-rich solid stream without most of the initial hemicellulose and cellulose to generate electrical power. The inlet stream is subject to drying at 87 °C to decrease the moisture on a wet basis to 10% [19], using air at ambient temperature and atmospheric pressure with a molar flow rate such that it supplies the stoichiometric quantity of O_2 for the conversion of solids in the following reactors. Then, the air outlet stream is compressed to a pressure of 60 bar [19] in a multistage compressor with three stages with an equal pressure ratio, which ensures that the pressure ratio is reasonable, and intermediate cooling at 35 °C and 65 °C to prevent the condensation of water. The dry solids and the compressed air are fed to an adiabatic gasification reactor, which is modeled by a stoichiometric reactor, where full conversion of solids, except ashes, to CO and H_2 takes place followed by a Gibbs reactor with H_2O , O_2 , N_2 , CO_2 , H_2 , CO , and CH_4 as possible products [19]. The gas outlet stream of this reactor is then fed to a turbine for electrical power generation, where the outlet pressure is 1 bar and the isentropic efficiency is 0.7 [19].

The reaction kinetics of the acid hydrolysis of hemicellulose to xylose at 100 °C in 2% w/w H_2SO_4 in water are given by the following expression for the reaction rate r [23]:

$$r = \alpha k_1 C, \quad (1)$$

with $\alpha = 0.554 \text{ g g}^{-1}$, $k_1 = 0.0246 \text{ min}^{-1}$, and hemicellulose concentration C in g L^{-1} .

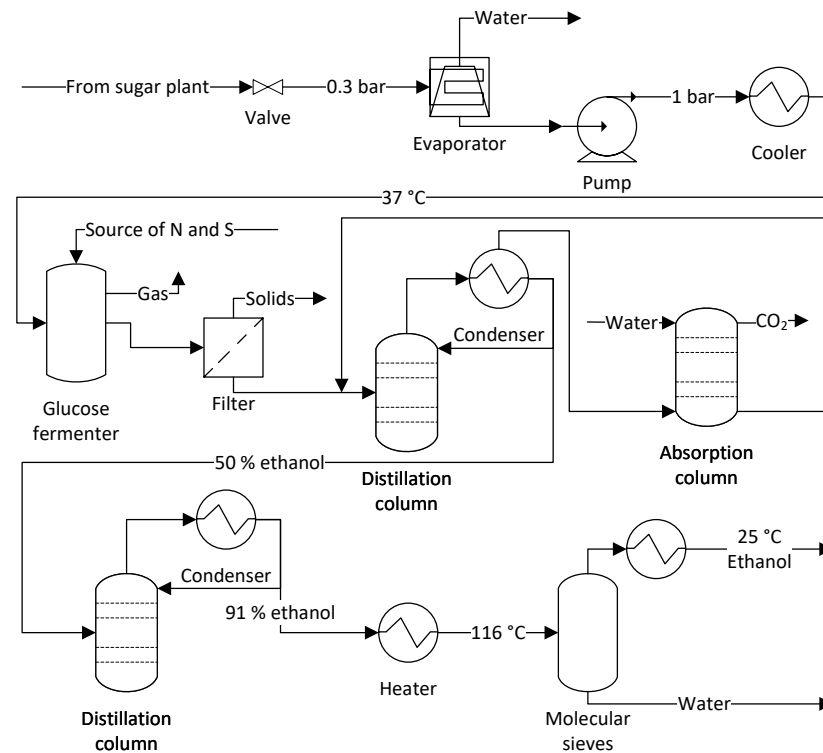


Figure 4. Schematic of the ethanol plant.

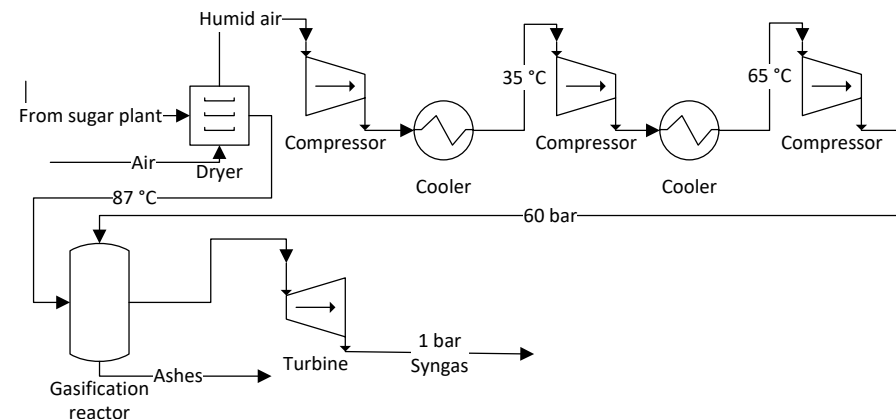


Figure 5. Schematic of the cogeneration plant.

Upon converting to the units of r in $\text{kmol m}^{-3} \text{s}^{-1}$ used by Aspen, the following expression is obtained:

$$r = 0.554 \text{ kg kg}^{-1} \times \frac{0.0246 \text{ min}^{-1}}{60 \text{ s min}^{-1}} \times \frac{C}{132.11612 \text{ kg kmol}^{-1}} = 1.719 \times 10^{-6} C. \quad (2)$$

The reaction kinetics of the enzymatic hydrolysis of cellulose to glucose at 50 °C without considering the formation of cellobiose are given by the following expression for the reaction rate r [24]:

$$r = 1.1116 \frac{k_{2r} E_{1b} C}{1 + \frac{S}{K_{2IG}}}, \quad (3)$$

with $k_{2r} = 7.10 \text{ mL mg}^{-1} \text{ h}^{-1}$, $E_{1b} = 50 \text{ mg mL}^{-1}$ [20], and $K_{2IG} = 0.01 \text{ mg mL}^{-1}$, and concentrations of cellulose C and glucose S in g L^{-1} .

Upon converting to the units of r in $\text{kmol m}^{-3} \text{ s}^{-1}$ used by Aspen, the following expression is obtained:

$$r = 1.1116 \times \frac{\frac{7.10 \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1}}{3600 \text{ s h}^{-1}} \times 50 \text{ kg m}^{-3} \times \frac{C}{180.15768 \text{ kg kmol}^{-1}}}{1 + \frac{S}{0.01 \text{ kg m}^{-3}}} = \frac{6.084 \times 10^{-4} C}{1 + e^{4.605 S}}. \quad (4)$$

The reaction kinetics of the formation of biomass and ethanol from glucose in glucose fermentation at 37°C are given by the following expressions for the rates of formation r_s , r_x , and r_p of glucose, biomass, and ethanol, respectively [27]:

$$r_x = \mu_{max} \frac{S}{K_s + S} \exp(-K_i S) \left(1 - \frac{X}{X_{max}}\right) \left(1 - \frac{P}{P_{max}}\right)^n X, \quad (5)$$

$$r_p = Y_{px} r_x + m_p X, \quad (6)$$

$$r_s = -\frac{r_x}{Y_x} - m_x X, \quad (7)$$

with $\mu_{max} = 0.426 \text{ h}^{-1}$, $X_{max} = 54.474 \text{ g L}^{-1}$, $P_{max} = 86.072 \text{ g L}^{-1}$, $Y_x = 9.763 \text{ g g}^{-1}$, $Y_{px} = 0.03831 \text{ g g}^{-1}$, $K_s = 4.1 \text{ g L}^{-1}$, $K_i = 0.002 \text{ L g}^{-1}$, $m_p = 0.1 \text{ h}^{-1}$, $m_x = 0.2 \text{ h}^{-1}$, $n = 1.5$, and concentrations of glucose S , biomass X , and ethanol P in g L^{-1} .

The expression for r_x is approximated as follows:

$$r_x = \mu_{max} \frac{S}{K_s + (1 + K_s K_i) S + K_i S^2} \left(1 - \frac{X}{X_{max}}\right) \left(1 - \frac{n}{P_{max}} P\right) X. \quad (8)$$

Upon converting to the units of r_s , r_x , r_p in $\text{kmol m}^{-3} \text{ s}^{-1}$ used by Aspen, the following expressions are obtained:

$$r_x = \frac{\frac{0.426 \text{ h}^{-1} \times S X}{3600 \text{ s h}^{-1} \times 23.23757 \text{ kg kmol}^{-1}} \left(1 - \frac{X}{54.474 \text{ kg m}^{-3}}\right) \left(1 - \frac{1.5P}{86.072 \text{ kg m}^{-3}}\right)}{4.1 \text{ kg m}^{-3} + (1 + 4.1 \times 0.002) S + 0.002 \text{ m}^3 \text{ kg}^{-1} \times S^2} = \frac{5.09233 \times 10^{-6} (S X (1 - e^{-3.99772} X - P(e^{-4.04972} - e^{-8.04744} X)))}{e^{1.41099} + e^{0.00816656 S} + e^{-6.21461 S^2}}, \quad (9)$$

$$r_p = \frac{\frac{0.426 \text{ h}^{-1} \times 0.03831 \times S X}{3600 \text{ s h}^{-1} \times 46.06904 \text{ kg kmol}^{-1}} \left(1 - \frac{X}{54.474 \text{ kg m}^{-3}}\right) \left(1 - \frac{1.5P}{86.072 \text{ kg m}^{-3}}\right)}{4.1 \text{ kg m}^{-3} + (1 + 4.1 \times 0.002) S + 0.002 \text{ m}^3 \text{ kg}^{-1} \times S^2} + \frac{0.1 \text{ h}^{-1} \times X}{3600 \text{ s h}^{-1} \times 46.06904 \text{ kg kmol}^{-1}} = \frac{9.84034 \times 10^{-8} (S X (1 - e^{-3.99772} X - P(e^{-4.04972} - e^{-8.04744} X)))}{e^{1.41099} + e^{0.00816656 S} + e^{-6.21461 S^2}} + 6.02960 \times 10^{-7} X, \quad (10)$$

$$\begin{aligned}
r_s = & - \frac{\frac{0.426 \text{ h}^{-1} \times SX}{3600 \text{ s h}^{-1} \times 9.763 \times 180.15768 \text{ kg kmol}^{-1}} \left(1 - \frac{X}{54.474 \text{ kg m}^{-3}}\right) \left(1 - \frac{1.5P}{86.072 \text{ kg m}^{-3}}\right)}{4.1 \text{ kg m}^{-3} + (1 + 4.1 \times 0.002)S + 0.002 \text{ m}^3 \text{ kg}^{-1} \times S^2} \\
& - \frac{0.2 \text{ h}^{-1} \times X}{3600 \text{ s h}^{-1} \times 180.15768 \text{ kg kmol}^{-1}} \\
= & - \frac{6.72777 \times 10^{-8} (SX(1 - e^{-3.99772}X - P(e^{-4.04972} - e^{-8.04744}X)))}{e^{1.41099} + e^{0.00816656}S + e^{-6.21461}S^2} \\
& - 3.08372 \times 10^{-7} X.
\end{aligned} \tag{11}$$

3. Results and Discussion

This work starts with the simulation of the process for the valorization of avocado waste biomass with the nominal conditions described for the process. To compute the results for the economic performance of the process, the costs of raw materials, products, and utilities are obtained as shown in Table 2, where the costs of utilities correspond to the ones provided by Aspen. According to Restrepo-Serna et al. [20], the cost of 0.022 USD/kg considered in Table 2 for avocado peel and seed corresponds to an estimated transport cost considering transport in a six-axle truck over 20 km. This means that the proposed biorefinery is assumed to be located in avocado-producing regions, where it is possible to take advantage of avocado waste biomass in the form of avocado peel and seed to produce valuable products. As a result, the estimated capital costs, operating costs including raw materials and utilities, and sales revenue for the nominal conditions are determined as shown in Table 3. It can be observed that a gross profit of approximately 30×10^6 USD/year is achieved for capital costs of USD 31.4×10^6 , where the gross profit corresponds to the difference between sales revenue and operating costs. Heat integration allows increasing the gross profit by 0.77×10^6 USD/year, owing to a smaller consumption of utilities. Figure 6 shows the composite curves that were used by Aspen Energy Analyzer to compute the energy and cost reduction targets owing to heat integration. It is possible to observe that most of the overlap between the hot and cold composite curves occurs at temperatures below 60°C , which means that a heat exchanger network for minimum energy requirements should focus on that temperature range. As can be seen in Figure 6, the energy savings amount to 9.4 MW for both hot and cold utilities, which corresponds to the horizontal overlap between the hot and cold composite curves, with the following distribution of utility savings: 9.1 MW of low-pressure steam, 0.3 MW of medium-pressure steam, 7.6 MW of cooling water, and 1.8 MW of refrigerant. To obtain these savings, the minimum temperature approach $\Delta T_{min} = 10 \text{ K}$ is considered, which results in the shifted composite curves, that is, the hot and cold composite curves with temperatures shifted by $-\Delta T_{min}/2$ and $\Delta T_{min}/2$, and the shifted temperatures of the utilities, that is, the temperatures of the hot and cold utilities shifted by $-\Delta T_{min}/2$ and $\Delta T_{min}/2$. Then, the savings for each utility are the difference between its original consumption and its target consumption, where (i) the original consumption of each hot/cold utility is given by the horizontal length of the cold/hot shifted composite curve below/above the shifted temperature of that utility that is not covered by another hot/cold utility with a lower/higher shifted temperature; and (ii) the target consumption of each hot/cold utility is given by the minimum horizontal distance between the cold and hot shifted composite curves above/below the shifted temperature of that utility that is not covered by another hot/cold utility with a lower/higher shifted temperature. This results in savings of 710.5×10^3 USD/year once the price of utilities is considered.

The following step is the identification of degrees of freedom for process optimization, which can then be used as decision variables for a numerical optimization problem. In this process, the variables with the most significant effect that are not determined by process constraints and specifications are the temperatures of the three adiabatic flash drums in the extraction plant. Since it is observed from Table 3 that the sales revenue and the costs of raw materials and utilities are more significant than the capital costs and other

operating costs that depend on them such as maintenance costs, the objective function of the numerical optimization problem to be maximized corresponds to the difference between the sales revenue and the costs of raw materials and utilities, which is used as a representation of gross profit. Although the information about capital costs, operating costs, and sales revenue enables the calculation of any desired profitability metric, the goal of the economic analysis in this paper is to allow decision making with respect to the values of relevant process variables based on economic criteria rather than providing a complete economic analysis of the proposed biorefinery. The reflux ratio and the number of stages of the distillation columns in the ethanol plant were not chosen as decision variables for numerical optimization since changes in the ethanol plant can only affect the costs of utilities and the sales revenue that results from the production of ethanol. As can be seen in Table 3 that details the different types of sales revenue, the costs of utilities and the sales revenue from ethanol are significantly smaller than the costs of raw materials and the sales revenue that results from other products, such as phenolic compounds. This means that the effect of optimization in the ethanol plant tends to be less important than the effect of optimization in the extraction plant since the latter one affects the flow rates of ethanol and CO₂ that can be recycled and avoid the costs of these raw materials and the flow rate of phenolic compounds that can be obtained as a product. The same reasoning is also valid for other possible decision variables related to the sugar and ethanol plants, such as the inlet concentration of glucose for the glucose fermenter in the sugar plant. In any case, variables such as the reflux ratio and the number of column stages of the distillation columns in the ethanol plant and the inlet concentration of glucose for the glucose fermenter in the sugar plant are suggested for future optimization studies with a greater focus on the sugar and ethanol plants of the biorefinery presented in this work. However, one must bear in mind that a larger number of decision variables may lead to larger computational cost and multiple local minima for the resulting nonlinear program, particularly in the case of discrete variables, such as the number of stages, which transform the problem into a mixed-integer nonlinear program. In summary, these challenges call for a sensible choice of decision variables.

The numerical methodology used for optimization corresponds to the LSSQP solver with the equation-oriented “Optimization” run mode of Aspen Plus. The tolerances correspond to the default options of the LSSQP solver, namely, a relative convergence tolerance of 0.0001 and a final constraint violation tolerance of 10^{-6} . The initial estimates are the values obtained for the simulation in nominal conditions. For successful process optimization, it was necessary to set upper or lower bounds for the temperatures of the three flash drums that were consistent with the utilities required to heat up or cool down the flash drum inlet streams. With these settings, optimization was performed without further difficulties.

Table 2. Costs of raw materials, products, and utilities.

Item	Value	Unit
CO ₂ [19]	0.01	USD/kg
Ethanol at 99.5% [19]	0.94	USD/kg
Water [19]	0.00125	USD/kg
2% w/w H ₂ SO ₄ in water [19]	0.02	USD/kg
2% w/v NaOH in water [19]	0.02	USD/kg
Avocado peel and seed [20]	0.022	USD/kg
Extractives [20]	10	USD/kg
Xylitol [19]	2.95	USD/kg
Syngas [20]	0.45	USD/kg
Cooling water	0.212×10^{-6}	USD/kJ
Refrigerant	2.74×10^{-6}	USD/kJ
Low-pressure steam	1.9×10^{-6}	USD/kJ
Medium-pressure steam	2.2×10^{-6}	USD/kJ
Electrical power	0.0775	USD/kWh

Table 3. Capital costs, operating costs including raw materials and utilities, and sales revenue for the nominal conditions and for the optimal conditions obtained via process optimization. The values in parentheses correspond to the cost reduction or profit increase owing to heat integration.

Item	Nominal Conditions	Optimal Conditions
Capital costs (USD 10 ³)	31,364.0	30,707.5
Operating costs (10 ³ USD/year)	22,843.2 (−767.3)	16,680.7 (−876.4)
Raw materials	13,111.1	7365.3
Utilities	4209.5 (−710.5)	4279.2 (−811.4)
Other	5522.6 (−56.8)	5036.2 (−65.0)
Sales revenue (10 ³ USD/year)	52,872.4	52,872.7
Phenolic compounds	12,274.0	12,274.3
Xylitol	22,340.5	22,340.5
Ethanol	1581.6	1581.6
Syngas	16,085.7	16,085.7
Electrical power	590.6	590.6
Gross profit (10 ³ USD/year)	30,029.2 (+767.3)	36,192.0 (+876.4)

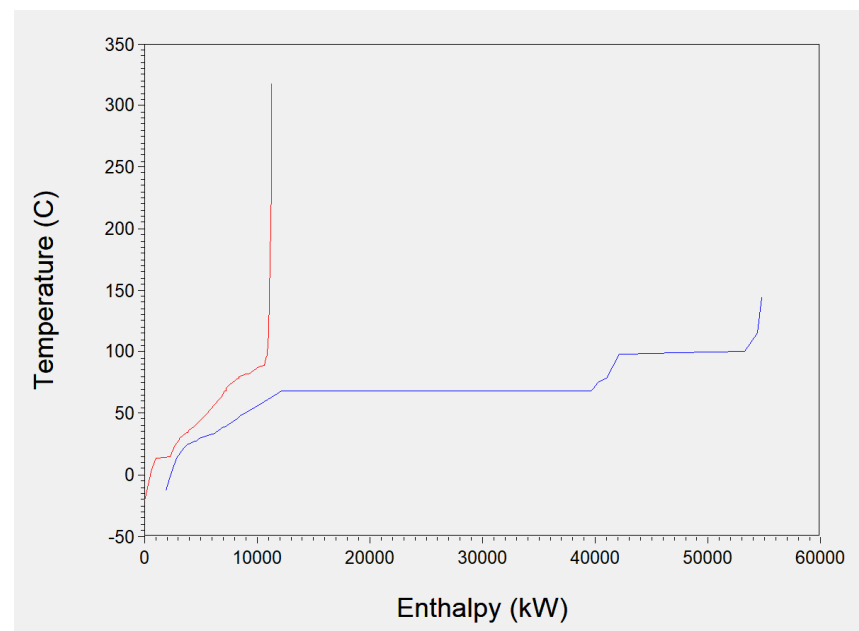


Figure 6. Composite curves (hot composite curve in red, cold composite curve in blue) used by Aspen Energy Analyzer to compute the energy and cost reduction targets owing to heat integration for the nominal conditions.

By optimizing the operating conditions, the results for the optimal conditions in Table 3 are obtained. As shown, the main beneficial effect of optimization is a reduction in the costs of raw materials, while the costs of utilities slightly increase. This effect is mainly caused by a very significant decrease in the costs of the supply of ethanol in the extraction plant, which is enabled by enhanced recovery of ethanol in the flash drums. In summary, the optimization results suggest the following changes in the operating conditions: in the first flash drum, the temperature should be as high as possible without increasing the hot utility costs too much so that more ethanol and CO₂ are vaporized, and the smallest possible quantities of ethanol and CO₂ are lost in the following flash drums; in the second flash drum, the temperature should be as low as possible without using temperatures below the ones in the rest of the process, which would require the introduction of cold utilities with lower temperature so that less ethanol is vaporized and released from the process in the vapor stream; and in the third flash drum, the temperature should be as high as possible without increasing the hot utility costs too much so that more ethanol is vaporized, and the smallest possible quantity of ethanol is released with the extractives in

the liquid stream. The use of more extreme temperatures in these flash drums leads to a slight increase in the costs of utilities. Table 4 summarizes the changes from the nominal operating conditions to the optimal ones. Also, the results show that this reduction in operating costs that results from optimization even leads to lower capital costs, which supports the choice of not including the capital costs in the objective function. In addition, the optimized conditions allow larger savings owing to heat integration, which can further reduce the operating costs. As a result, a gross profit of 37×10^6 USD/year is reached for capital costs of USD 30.7×10^6 .

Table 4. Nominal operating conditions and optimal conditions obtained via process optimization. *T* denotes temperature.

Variable	Nominal Conditions	Optimal Conditions
<i>T</i> of first flash drum (°C)	67.5	112.1
<i>T</i> of second flash drum (°C)	14	−20.0
<i>T</i> of third flash drum (°C)	80	131.8

4. Conclusions

In this work, the detailed modeling, simulation, and optimization of a biorefinery for processing avocado peel and seed to produce value-added products, such as phenolic compounds, bioethanol, biological xylitol, syngas, and electrical power, was considered. The novel aspects of this work are the use of an equation-oriented framework for process modeling, simulation, and optimization via Aspen Plus; the detailed description of all the process specifications; and the use of process optimization and heat integration to obtain the optimal operating conditions. As a result of the combined effect of process optimization and heat integration, it was possible to improve the gross profit obtained by the biorefinery from approximately 30×10^6 USD/year for capital costs of USD 31.4×10^6 to a gross profit of 37×10^6 USD/year for capital costs of USD 30.7×10^6 .

In future work, other by-products of avocado production can also be considered to extend the techno-economic analysis of a biorefinery based on avocado waste, such as avocado pomace, starch from avocado seed, protein from avocado pulp, or natural orange dyes. Also, the current study represents a first step toward the modeling and optimization of a superstructure of a biorefinery for avocado processing, which will include different alternatives for each stage of the process or even alternative products and combinations with other types of biological waste. This will allow deciding the best configuration for avocado-based biorefineries to be implemented in the future.

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Appendix A. Configuration of Equation-Oriented Mode in Aspen Plus

The settings in Table A1 were used in the “EO Configuration” option “Spec Groups”, which means that the calculated variable is adjusted such that the constant variable equals the specified value.

Table A1. Settings in the “EO Configuration” option “Spec Groups”.

Calculated Variable	Constant Variable	Value (Units)
AIRIN.BLK.MASS	DRY.AIROUT.STR.O2	0.194747 (-)
CO2IN.BLK.MASS	R1.BLK.EXT-2_MASS	30,198.5 (kg h ⁻¹)
ETOHN.BLK.MASS	R1.BLK.EXT-3_MASS	4110.50 (kg h ⁻¹)
R1.BLK.CONV_RXN_1_CISOLID_PHE	R1.BLK.EXT-1_MASS	153.459 (kg h ⁻¹)
XF.BLK.CONV_RXN_1_XYLOSE	XFS.BLK.XFO_XYLITOL	0.00693201 (-)
XFFH.BLK.XFFI_VAPOR_FRACTION	XFH.BLK.XFI_XYLOSE	0.00878562 (-)
ETOH.C.BLK.ETOH_MASS_FLOW	CM.BLK.CLI_ETOH	0.396505 (-)
CFH.BLK.CFI_VAPOR_FRACTION	CM.BLK.CLI_H2O	0.14485 (-)
GFFH.BLK.GFFI_VAPOR_FRACTION	GFH.BLK.GFI_GLUC	0.0053653 (-)
NAOH.BLK.MOLES	NR.BLK.NRO_H2SO4	2.90552×10^{-9} (-)

The settings in Table A2 were used in the “EO Configuration” option “Connection”, which means that the destination variable is equal to the source variable times the scale value.

Table A2. Settings in the “EO Configuration” option “Connection”.

Destination Variable	Source Variable	Scale
CO2R.BLK.TEMP	CO2S.BLK.CO2R-0_TEMP	1
CO2R.BLK.PRES	CO2S.BLK.CO2R-0_PRES	1
CO2R.BLK.MASS	CO2S.BLK.CO2R-0_MASS	1
CO2R.BLK.ETOH_MOLE_FRAC	CO2S.BLK.CO2R-0_ETOH	1
CO2R.BLK.CO2_MOLE_FRAC	CO2S.BLK.CO2R-0_CO2	1
CO2R.BLK.PHE-L_MOLE_FRAC	CO2S.BLK.CO2R-0_PHE-L	1
ETHR.BLK.TEMP	ETHC.BLK.ETHR-0_TEMP	1
ETHR.BLK.PRES	ETHC.BLK.ETHR-0_PRES	1
ETHR.BLK.MASS	ETHC.BLK.ETHR-0_MASS	1
ETHR.BLK.ETOH_MOLE_FRAC	ETHC.BLK.ETHR-0_ETOH	1
ETHR.BLK.CO2_MOLE_FRAC	ETHC.BLK.ETHR-0_CO2	1
ETHR.BLK.PHE-L_MOLE_FRAC	ETHC.BLK.ETHR-0_PHE-L	1
VDR.BLK.TEMP	C1.VDR-0.STR.TEMP	1
VDR.BLK.PRES	C1.VDR-0.STR.PRES	1
VDR.BLK.MOLES	C1.VDR-0.STR.MOLES	1
VDR.BLK.H2O_MOLE_FRAC	C1.VDR-0.STR.H2O	1
VDR.BLK.ETOH_MOLE_FRAC	C1.VDR-0.STR.ETOH	1
VDR.BLK.O2_MOLE_FRAC	C1.VDR-0.STR.O2	1
VDR.BLK.N2_MOLE_FRAC	C1.VDR-0.STR.N2	1
VDR.BLK.CO2_MOLE_FRAC	C1.VDR-0.STR.CO2	1
VDR.BLK.SO2_MOLE_FRAC	C1.VDR-0.STR.SO2	1
H2SO4.BLK.MASS	AM.BLK.AMO_CISOLID_MASS	10
XFH2O.BLK.H2O_MOLE_FLOW	XF.BLK.NET_GEN_XYLITOL	1
H2O.BLK.MASS	EM.BLK.EMO_CISOLID_MASS	13.28571429
GASAIR.BLK.MOLES	GAS.BLK.NET_GEN_O2	-4.761904762
SES.BLK.ES_MASS	SES.BLK.ES_CISOLID_MASS	10 ⁻⁷
SAS.BLK.AS_MASS	SAS.BLK.AS_CISOLID_MASS	10 ⁻⁷
SRS.BLK.RS_MASS	SRS.BLK.RS_CISOLID_MASS	10 ⁻⁷
SGS.BLK.GS_MASS	SGS.BLK.GS_CISOLID_MASS	10 ⁻⁷
SNS.BLK.NS_MASS	SNS.BLK.NS_CISOLID_MASS	10 ⁻⁵

These settings were used to implement the following specifications:

- DRY.AIROUT.STR.O2: to ensure that the mass flow rate of air is the required one to achieve 100% of relative humidity in the air outlet stream of the dryer DRY at 40 °C in the extraction plant, which implies that the corresponding mole fraction of O₂ in the humid air stream (AIROUT) is 0.194747.

- R1.BLK.EXT-2_MASS: to ensure that a mass flow ratio of 11.02 g of CO₂ per g of solids at the inlet of the extractor R1 is achieved, which implies that the mass flow rate of the CO₂ outlet stream of the extractor (EXT-2) is equal to $11.02 \times 2740.335 = 30,198.5 \text{ kg h}^{-1}$, where $2740.335 \text{ kg h}^{-1}$ is the mass flow rate of solids (avocado peel and seed) after a reduction in the moisture on a wet basis to 5.12%.
- R1.BLK.EXT-3_MASS: to ensure that a mass flow ratio of 1.5 g of ethanol per g of solids at the inlet of the extractor R1 is achieved, which implies that the mass flow rate of the ethanol outlet stream of the extractor (EXT-3) is equal to $1.5 \times 2740.335 = 4110.50 \text{ kg h}^{-1}$, where $2740.335 \text{ kg h}^{-1}$ is the mass flow rate of solids (avocado peel and seed) after a reduction in the moisture on a wet basis to 5.12%.
- R1.BLK.EXT-1_MASS: to ensure that the conversion of extractives in the solids to extractives in the fluid phase is such that an extraction yield of 5.6% with respect to the mass flow rate of solids at the inlet of the extractor R1 is achieved, which implies that the mass flow rate of the extractives outlet stream of the extractor without recycled extractives (EXT-1) is equal to $0.056 \times 2740.335 = 153.459 \text{ kg h}^{-1}$, where $2740.335 \text{ kg h}^{-1}$ is the mass flow rate of solids (avocado peel and seed) after a reduction in the moisture on a wet basis to 5.12%.
- XFS.BLK.XFO_XYLITOL: to ensure that the conversion of xylose and water to xylitol and oxygen in the xylose fermenter at 30 °C is such that a xylose productivity of $0.58 \text{ g L}^{-1} \text{ h}^{-1}$ in 96 h of fermentation is achieved for the liquid phase after separation in a gas-liquid separator XFS at the outlet of the xylose fermenter, which implies that, when the inlet stream of the xylose fermenter with a concentration of 70 g L^{-1} of xylose is converted into a liquid outlet stream of the xylose fermenter (XFO) with a concentration of $0.58 \times 96 = 55.68 \text{ g L}^{-1}$ of xylitol, the resulting mole fraction of xylitol is 0.00693201.
- XFH.BLK.XFI_XYLOSE: to ensure that a concentration of 70 g L^{-1} of xylose is reached at the outlet of the heater XFH that is fed to the xylose fermenter, which implies that the mole fraction of xylose in the inlet stream of the xylose fermenter (XFI) is $\left(\frac{1}{150.1314} \frac{70}{1017.682} + \frac{1}{18.01528} \left(1 - \frac{70}{1017.682} \right) \right)^{-1} \left(\frac{1}{150.1314} \frac{70}{1017.682} \right) = 0.00878562$, where $150.1314 \text{ g mol}^{-1}$ is the molecular weight of xylose, $18.01528 \text{ g mol}^{-1}$ is the molecular weight of water, and $1017.682 \text{ g L}^{-1}$ is the mass density of an aqueous solution with a concentration of 70 g L^{-1} of xylose.
- CM.BLK.CLI_ETOH, CM.BLK.CLI_H2O: to ensure that a mass fraction of 0.875 of ethanol in the water/ethanol solvent is achieved at the outlet of the mixer CM that is fed to the crystallizer inlet, and a solvent to xylitol/xylose mass ratio of 0.3 is achieved at the crystallizer outlet, which implies that the mole fractions of ethanol and water in the liquid crystallizer inlet (CLI) are $\left(\frac{1}{152.14728} + \frac{0.262956}{150.1314} + \frac{0.125 \times 0.3 \times 1.262956}{18.01528} + \frac{0.875 \times 0.3 \times 1.262956}{46.06904} \right)^{-1} \frac{0.875 \times 0.3 \times 1.262956}{46.06904} = 0.396505$ and $\left(\frac{1}{152.14728} + \frac{0.262956}{150.1314} + \frac{0.125 \times 0.3 \times 1.262956}{18.01528} + \frac{0.875 \times 0.3 \times 1.262956}{46.06904} \right)^{-1} \frac{0.125 \times 0.3 \times 1.262956}{18.01528} = 0.14485$, respectively, where 0.262956 is the mass flow ratio of xylose to xylitol at the inlet of the mixer CM, $152.14728 \text{ g mol}^{-1}$ is the molecular weight of xylitol, $150.1314 \text{ g mol}^{-1}$ is the molecular weight of xylose, $18.01528 \text{ g mol}^{-1}$ is the molecular weight of water, and $46.06904 \text{ g mol}^{-1}$ is the molecular weight of ethanol.
- GFH.BLK.GFI_GLUC: to ensure that a concentration of 51.29 g L^{-1} of glucose is reached at the outlet of the heater GFH that is fed to the glucose fermenter, which implies that the mole fraction of glucose in the inlet stream of the glucose fermenter (GFI) is $\left(\frac{1}{180.15768} \frac{51.29}{1002.102} + \frac{1}{18.01528} \left(1 - \frac{51.29}{1002.102} \right) \right)^{-1} \left(\frac{1}{180.15768} \frac{51.29}{1002.102} \right) = 0.0053653$, where $180.15768 \text{ g mol}^{-1}$ is the molecular weight of glucose, $18.01528 \text{ g mol}^{-1}$ is the molecular weight of water, and $1002.102 \text{ g L}^{-1}$ is the mass density of an aqueous solution with a concentration of 51.29 g L^{-1} of glucose.

- NR.BLK.NRO_H2SO4: to ensure that the pH at the outlet of the neutralization reactor NR is increased to 6.5, which implies that the mole fraction of H₂SO₄ in the outlet stream of the neutralization reactor (NRO) is $\frac{10^{-6.5}}{2 \times 54.4184} = 2.90552 \times 10^{-9}$, where 54.4184 mol L⁻¹ is the molar density of the outlet stream of the neutralization reactor, where H₂SO₄ reacts with NaOH to form water and Na₂SO₄.
- CO2R.BLK.TEMP, CO2R.BLK.PRES, CO2R.BLK.MASS, CO2R.BLK.ETOH_MOLE_FRAC, CO2R.BLK.CO2_MOLE_FRAC, CO2R.BLK.PHE-L_MOLE_FRAC: to ensure that the assumed recycled CO₂-rich stream is equal to the computed CO₂-rich stream from the CO₂ separator CO2S, namely, with respect to its temperature, pressure, mass flow rate, and mole fractions of ethanol, CO₂, and phenolic compounds in the fluid phase.
- ETHR.BLK.TEMP, ETHR.BLK.PRES, ETHR.BLK.MASS, ETHR.BLK.ETOH_MOLE_FRAC, ETHR.BLK.CO2_MOLE_FRAC, ETHR.BLK.PHE-L_MOLE_FRAC: to ensure that the assumed recycled ethanol-rich stream is equal to the computed ethanol-rich stream from the ethanol condenser ETHC, namely, with respect to its temperature, pressure, mass flow rate, and mole fractions of ethanol, CO₂, and phenolic compounds in the fluid phase.
- VDR.BLK.TEMP, VDR.BLK.PRES, VDR.BLK.MOLES, VDR.BLK.H2O_MOLE_FRAC, VDR.BLK.ETOH_MOLE_FRAC, VDR.BLK.O2_MOLE_FRAC, VDR.BLK.N2_MOLE_FRAC, VDR.BLK.CO2_MOLE_FRAC, VDR.BLK.SO2_MOLE_FRAC: to ensure that the assumed vapor distillate of the first distillation column C1 in the ethanol plant is equal to the computed vapor distillate from the first distillation column in the ethanol plant, namely, with respect to its temperature, pressure, mole flow rate, and mole fractions of H₂O, ethanol, O₂, N₂, CO₂, and SO₂.
- H2SO4.BLK.MASS: to ensure that the mass flow rate of the diluted H₂SO₄ stream is 10 times the mass flow rate of solids in the mixer AM at the inlet of the acid hydrolysis reactor.
- XFH2O.BLK.H2O_MOLE_FLOW: to ensure that the mass flow rate of water fed to the xylose fermenter is the one that is strictly needed for the required production of xylitol in the fermenter XF.
- H2O.BLK.MASS: to ensure that the solid stream in the mixer EM at the inlet of the enzymatic hydrolysis reactor is mixed with water to achieve a mass fraction of solids of 7%, which implies that the mass flow rate of water is $\frac{0.93}{0.07} = 13.28571429$ times the flow rate of solids.
- GASAIR.BLK.MOLES: to ensure that the molar flow rate of air that is fed to the dryer at the inlet of the gasification reactor supplies the stoichiometric quantity of O₂ for the conversion of solids in the adiabatic gasification reactor GAS, which implies that the molar flow rate of air is $-\frac{1}{0.21} = -4.761904762$ the net generation of O₂ in the reactor, where 0.21 is the mole fraction of O₂ in the air.
- SES.BLK.ES_MASS, SAS.BLK.AS_MASS, SRS.BLK.RS_MASS, SGS.BLK.GS_MASS, SNS.BLK.NS_MASS: to ensure that the solids are fully separated with a liquid load of 10⁻⁷ in the solid outlet streams ES, AS, RS, and GS of the filters SES, SAS, SRS, and SGS at the outlet of the enzymatic hydrolysis reactor, acid hydrolysis reactor, extraction plant, and glucose fermenter, respectively, and 10⁻⁵ in the solid outlet stream NS of the filter SNS at the outlet of the neutralization reactor.

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