

# Technoeconomic analysis of broccoli biorefineries for polyphenol extraction and biobutanol production

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Received: June 12, 2022

Accepted: September 15, 2022

Published: September 25, 2022

DOI: <https://doi.org/10.56845/rebs.v4i1.70>

**Abstract:** Fossil resources dominate the energy supply. In 2019, the total energy supply worldwide accounted for 606 exajoules (EJ), of which fossil fuels (oil, coal, and gas) had a share of 81% (490 EJ). The biorefinery concept proposes the synthesis of renewable energies as an alternative to fossil carburants. As a second-generation biofuel, biobutanol has outstanding characteristics and can be obtained from agricultural residues and organic wastes; however, its bioprocessing is not economically feasible using current methodologies. In 2021, the global production of broccoli (*Brassica oleracea var. Italica*) was 25.5 million tons; being the fifth top producer, Mexico generated 687,000 tons of this vegetable. In this work we propose a production design for the synthesis of biobutanol and the recovery of valuable byproducts, like high-value polyphenolic compounds, from broccoli residues, abundant in the state of Guanajuato, Mexico. For the transformation of the substrate a biochemical matrix was proposed for its composition, as well as a biotechnological route that follows a general path with the acid pretreatment of biomass, enzymatic hydrolysis, and acetone-biobutanol-ethanol (ABE) fermentation using anaerobic bacteria. The outlined biorefinery integrates conventional methods in three methodological pathways and a hybrid model for the downstream process. With the aim of visualizing the global economic performance and evaluating a possible reduction in production costs, we performed a technoeconomic analysis of the designed second generation biorefinery plant. The economic evaluation was carried out using SuperPro Designer® V 12.0. The results confirm the enormous dependence that this type of biorefinery suffers from energy demands. We found that by implementing strategic adaptations to the downstream process operating costs can be considerably reduced. However, to achieve full financial efficiency in the production of biobutanol from broccoli residues, it is necessary to deepen the research and development of innovative methods to efficiently separate and purify the final products, as well as novel methodologies for the biotransformation of the described lignocellulosic biomass along the entire technological route. We also found that there is a large opportunity in the valorization of the plentiful broccoli residues generated in the Guanajuato region.

**Keywords:** biofuels; biobutanol; bioprocesses; biocircularity, sustainability

## Introduction

In 2019, 490 EJ of energy came from fossil sources worldwide, which accounted for 81% of the global energy supply (606 EJ). In the same period, 121 EJ of energy was consumed in the transport sector, with crude oil and its derivatives contributing 91.3% of its demand (110.5 EJ), while liquid biofuels (mainly bioethanol and biodiesel) provided only 3.99 EJ to the sector, for a share of 3.3% (IEA, 2021; WBA, 2021; IRENA, 2022). Biorefining is being studied with the aim of configuring efficient and economically viable production methods for the synthesis of fuels derived from renewable sources (De Buck *et al.*, 2020). A biorefinery could be seen as a facility destined to upgrade biomass in different products such as chemicals, energy vectors, and high-value-added compounds (Solarte & Cardona, 2021). Biorefineries have been classified based on the type of feedstocks used, the type of intermediates generated (syngas or sugar), conversion processes (thermochemical, biochemical, two platforms), and the status of technology execution, i.e., conventional or advanced (Takkellapati *et al.*, 2018). However, the production system of biorefineries is categorized based on four key characteristics: raw materials, pretreatments, platforms, and products, and so these four characteristics can be combined in a diversity of processes to create a variety of biorefinery concepts with various processing arrangements. Nevertheless, biorefineries can be further divided into two types based on the products they produce: energy-driven and material-driven biorefinery systems. In an energy-driven biorefinery system, biomass is primarily used to produce biofuels, energy, and heat. A material-driven biorefinery, on the other hand, produces bio-based products like platform chemicals and other biomaterials. In both systems process residues can be used to generate electricity, reducing waste generation. A biorefinery's economic performance is influenced by a diversity of design factors, including location, raw material, conversion technology, and end products (Reshmy *et al.*, 2022). In 2021, 408 biorefineries were in operation worldwide, 298 of them in the EU and 110 in the rest of the world. Only 26 of these plants operate with lignocellulosic waste and only 18 have liquid biofuels as their productive objective (Baldoni *et al.*, 2021; European Commission, 2021).

Millions of tons of agricultural residues generated globally each year can be used to produce biofuels (FAO, 2017), and lignocellulosic agricultural biomasses are abundant, renewable, and very attractive resources for their production in large scale (Philippini *et al.*, 2020). Global biofuel markets are dominated by first-generation bioethanol and biodiesel (mainly produced from dedicated sugar cane and corn), which are in the nascent stages of commercialization, but biobutanol has outstanding advantages over them (Yusoff *et al.*, 2015). While biobutanol is still in the laboratory/pilot production phase, it is almost as energy dense (29.2 MJ/dm<sup>3</sup>) as gasoline; that is, it has 50% more energy density than bioethanol (19.6 MJ/dm<sup>3</sup>), consequently offering lower consumptions per mileage (Bankar *et al.*, 2013; Mahapatra & Kumar, 2017). In addition, its lower volatility, lower heat of vaporization (0.43 MJ/kg vs 0.92 MJ/kg) and higher flash point (relative to bioethanol) make it potentially safer when considering transportation and use at high temperatures. Also, its higher viscosity and lubricity may potentially protect components of the engine that have direct contact with fuel against wear problems (Trindade & Gonçalves, 2017). Biobutanol is also less corrosive and has a less hygroscopic nature, and therefore can be easily transported in pipelines as compared to ethanol. These properties assist in the long ignition delay, proper fuel-air mixing, and lower NO<sub>x</sub> and soot emissions with biobutanol use in internal combustion engines (Civelek *et al.*, 2019). Biobutanol is a “drop in” biofuel which can be blended with gasoline up to 85% and can be used in vehicles without any modifications; blends up to 16% and 15% are allowed in the United States and Europe, respectively (Tsong-Yu *et al.*, 2020). Due to these remarkable characteristics, it is reasonable to consider that biobutanol presents alluring advantages as a substitute for gasoline and other renewable fuels present in the energy markets.

The conventional production of biobutanol by the ABE fermentation process (with the bacteria strain *Clostridium acetobutylicum*) still presents insuperable challenges because the mechanics of its purification, carried out by distillation units, is energy and cost intensive (Li *et al.*, 2021). To this day, no biorefinery in the world produces second generation biobutanol from cellulosic residues. However, some high-tech companies are leading efforts to develop novel methods to produce it. Huge investments are being done and there are some pilot plants and projects producing renewable biobutanol from lignocellulosic residues and nonconventional feedstock. Two major players in biobutanol innovation are Celtic Renewables and Phytonix, which use their own biotech with the objective to produce renewable butanol at a commercial scale. Celtic Renewables, an awarded biotech company based in Scotland, has recently built a biorefinery where it will use ABE fermentation and its own biotechnology to produce biobutanol from residues of the whisky industry, with the hope to achieve commercial status soon (Celtic Renewable, 2022). Phytonix, a firm based in the United States, has engineered new strains of cyanobacteria which use photosynthesis to convert CO<sub>2</sub> into biobutanol and other higher alcohols. Its globally patented process employs (photosynthetic) cyanobacteria engineered via synthetic biology. The firm is currently testing and optimizing its production process at pilot scale (Phytonix, 2022).

Numerous studies have addressed the production of biobutanol from lignocellulosic biomass and a variety of crops. Generally, the common conclusion they all tend to share is that the high production costs and low biobutanol titers make its production expensive for large-scale practical applications. Therefore, biobutanol produced by *Clostridium*, the traditional technology for its synthesis, cannot compete with petrochemical butanol. Also, a common conclusion suggests that production technologies along the entire process, as well as highly efficient microbial consortiums need to be improved to make biobutanol production economically feasible (Mahapatra & Kumar, 2017; Jiang *et al.*, 2019; Tsong-Yu *et al.*, 2020; Birgen *et al.*, 2021; Tiginova *et al.*, 2021; Veza *et al.*, 2021; Guo *et al.*, 2022). To the best of our knowledge, there is no previous work dealing with the production of biobutanol from broccoli as feedstock. However, there are studies that report research on the synthesis of second generation biofuels (like biobutanol) and recovery of byproducts from different lignocellulosic crops with the approach of process simulation, commonly using chemical engineering software packages such as SuperPro Designer<sup>®</sup> and Aspen Plus<sup>®</sup>, and technoeconomic analysis (Quintero *et al.*, 2013; Procentese *et al.*, 2014; Sanchez *et al.*, 2017; Haigh *et al.*, 2018; Li *et al.*, 2020; Scown *et al.*, 2021).

Polyphenols are a large group of antioxidant compounds present in considerable amounts in many vegetables and fruits (Bhandari & Kwak, 2015). Polyphenols are valuable molecules for the pharmaceutical and food industries as they are known to be strong antioxidants and disease preventives. Epidemiological studies have reported a positive correlation between vegetable intake and a decrease in the rate of cardiovascular disease, aging, certain cancers, and other degenerative diseases related to oxidative stress, which is attributed to the antioxidant activity of phenolic compounds in vegetables (Safdar *et al.*, 2016). Numerous studies also suggest that these bioactive molecules lower the risk of chronic inflammations and may also have an impact on the diversity of the gut microbiota. Leafy green vegetables usually contain high levels of phenolic compounds. In Brassica vegetables, including broccoli, many phenolic

compounds have been identified in the tissues not used as food, such as the leaves and stems (Berndtsson *et al.*, 2020). Therefore, broccoli leaf and stem tissues can be a good source of these high-value biomolecules (Liu *et al.*, 2018).

Mexico is the fifth largest producer of broccoli in the world. With 67% of the national production (687,000 tons), the central state of Guanajuato produces 482,000 tons of broccoli and generates some 1,500,000 tons of residues per year, which could be processed for the synthesis of biobutanol (SIAP, 2021; TRIDGE, 2020). This work reports the results of a study that examines the technoeconomic feasibility of a theoretical design for an energy-driven second-generation biorefinery that processes broccoli agricultural wastes to produce biobutanol and high-value compounds, especially polyphenols. Three process configurations that implement some operative variations and two purification approaches were studied. The technoeconomic and production analysis were evaluated using the cost and estimation methods built into the platform of SuperPro Designer® V 12.0.

## Materials and Methods

This study considered a dried mixture of broccoli leaves and stems as the raw material considering the following composition: 40% cellulose, 34% hemicellulose, 10% lignin, 5.5% lipids, 10% ashes and 0.5% polyphenols (Campas *et al.*, 2009; Madhu & Kochhar, 2014; Navarro *et al.*, 2016; Thomas *et al.*, 2018; Wadmare *et al.*, 2019). A technological pathway was proposed for its transformation to biobutanol, obtaining valuable byproducts such as a polyphenol broth, lignin, and carbon dioxide (for beverage and food industries). Next, a technological pathway was defined by integrating the stages, unit operations, streams, etc. The process is composed of seven operating stages as follows: Mechanical Reduction (RED), Polyphenol Extraction (EXT), Pretreatment (PRT), Fermentation Inhibitor Detoxification (DTX), Saccharification (SAC), Fermentation (ABE) and Separation and Purification (S&P). With the purpose of obtaining results that are consistent with a logical operational reality, a key point considered in this work was the conversion efficiency for each of the stages, as reported in the available literature (Lopez *et al.*, 2010; Kaminski *et al.*, 2011; Kraemer *et al.*, 2011; Visioli *et al.*, 2014; Kujawska *et al.*, 2015; Jovanović *et al.*, 2017; Maroun *et al.*, 2018; Kumar *et al.*, 2020; Birgen *et al.*, 2021; Phillips, 2021; Veza *et al.*, 2021). Finally, assisted by SuperPro Designer® (SPD), the operational template for the plant and its process was integrated. For the evaluation of the biorefinery/production the base scenario considers several process capacities i.e., 100, 500 and 1,000 tons/day with three different configurations: i) Biorefining with Conventional Distillation (BCD), fitted out with a traditional distillation train for the S&P stage; ii) Hybrid Biorefining with Extraction (HBE), which integrates an extraction unit that operates with mesitylene as a solvent, intended to separate the large water contents from the fermentation broth before distillation with the aim of potentially reducing purification costs and iii) Hybrid Biorefining eliminating Polyphenol Extraction (HBEB), which implements the latter extraction strategy for the S&P stage but eliminates the step of polyphenol recovery (EXT), in an exercise to review the benefits of cutting production costs at the expense of a dispensable stream (polyphenol broth), which was thus phased out. For each plant capacity, a process evaluation was performed by iterating small increments in production. Figure 1 outlines the block diagrams with the production stages and desired products of the biorefinery in its three alternatives. The economic analysis was performed considering: Total Capital Investment (TCI), Net Operating Costs (NOC), Total Revenue (TR) and energy consumptions by Net Present Value techniques. The cost of energy and raw materials was automatically calculated by the SuperPro Designer® platform according to the integrated economic update system, while the sale price of the products was taken according to the most up-to-date index (Chemanalyst, 2022). The cost of *Clostridium* was set at 5% of the total income from biobutanol sales. The labor cost was also estimated by the simulation software and was then adjusted to the Mexican labor market, considering an index of 0.217 as proposed by the best estimates from related industrial and labor institutes (IVEMNSA, 2022; Trading Economics, 2022). The technoeconomic analyses were estimated in USD with proper adjustments for service costs in Mexico. For the simulation, the production was modeled as a continuous process. Table 1 lists all the prices considered in this work.

### Process description

The designed process considered this path: the feed biomass, previously dehydrated, is physically reduced to a particle diameter of 0.5 mm using a bulk flow shredder (unit process 1), then flown through a vibrating screen (2) that recirculates the noncompliant granules (> 0.5 mm) through a pneumatic conveyor (3) and back to the mill, mixing them with the feed stream (4). The reduced solid feedstock is then heated (5) and conducted by a screw conveyor (for simplicity not considered for calculations in this study) to the next operating module. For the extraction of polyphenols, the material is diluted to a 1:5 ratio (w/v) in a 50% (v/v) aqueous solution of methanol and heated at 90°C for one hour

in a mixing tank (6); at the end of this process the mixture is filtered and separated (7). The filtered fraction is subjected to flash evaporation (8) to recover 90% of the water and send it as a vapor flow to a heat exchanger (5). In the bottom stream, a mixture of polyphenols, lipids, and ash is produced as a recovery broth for the desired polyphenols (a marketable byproduct). The retained fraction, rich in methanol and biopolymers (celluloses, hemicelluloses, and lignin) is rotary dried (9) with steam to recover the methanol, which is recycled into the process. Its bottom stream, a solid concentrate of lignocellulosic polymers is sent to a stirred reactor (10) for pretreatment, being subjected to a sulfuric acid solution diluted to 1% (v/v), in a ratio of 1:10 (w/v) and brought to 135°C for 3½ hours. This process increases both the biomass porosity and the susceptibility of the celluloses to enzymatic hydrolysis. It also allows the conversion of hemicelluloses to pentoses (xyloses), yielding a hydrolysate that contains, in addition to the celluloses and lignin, potentially inhibitory hemicellulose derivatives (for consequent fermentation operations), i.e.: acetic acid, furfural, hydroxymethylfurfural (HMF) and others. To eliminate these inhibitors, the hydrolysate is subjected to detoxification with Ca(OH)<sub>2</sub> at 60°C for half an hour in a stirred reactor (11). This reaction produces a solid gypsum (CaSO<sub>4</sub>), which is eliminated by filtration (12) to obtain a mixture containing biopolymers and polysaccharides (pentoses and hexoses). This stream is concentrated by evaporation (13), removing 80% of its water content as steam and then recirculating it to the downstream process (heat exchangers in S&P operations). To convert polysaccharides into glucose the stream is brought under the action of cellulase enzymes (Cellic® CTec3) in a stirred reactor (14) with a proportion of 1:100 (enzymes-substrate) at 45°C for 68 hours. At the end of saccharification, the mixture is now vacuum filtered (15) and separated into a flux of lignin as a byproduct to be marketed, and a concentrated stream of glucose. This current is directed to the fermentation stage and exposed to the action of bacteria (*Clostridium*) in a biological reactor (16) with a ratio of 100:1, under anaerobic conditions at 45 °C and 36 h. The fermentation (ABE) produces CO<sub>2</sub> emissions, which are recovered to be marketed, and yields an aqueous mixture (at 30.82 g/L) of acetone, butanol, and ethanol in a 3:6:1 ratio, as well as a residual fraction of proteins, lipids, traces of organic acids and cells (fermentation microorganisms), which is removed by vacuum filtration (17). The concentrated ABE liquor is sent to the next phase for disposal in separate streams of acetone, butanol, and ethanol.

Table 1. Price Economics.

Raw material	Costs (\$/kg)
Broccoli residues (50%, leaf/stem)	0.05
Ca(OH) <sub>2</sub>	0.11
H <sub>2</sub> SO <sub>4</sub>	0.07
Enzyme	0.04
Methanol	0.03
Products	Costs (\$/kg)
Polyphenols (low purity mixture)	0.2
Lignin	0.74
CO <sub>2</sub>	0.0079
Butanol	1.48
Acetone	0.72
Ethanol	0.75

Avg Labor Cost (operatives and management): 15 USD/h

Chemanalyst, 2022; IVEMNSA, 2022; Trading Economics, 2022, & SPD®

### Separation and Purification Approaches

The S&P stage integrated in the BCD strategy uses a decanter and a sequence of distillation columns (Patracu *et al.*, 2017). The separation process begins by decanting (18) a stream fraction rich in butanol and sending it to a column (21) that produces highly pure biobutanol (99.97%) as the bottom effluent, and a stream of water that is recycled (to the decanter). The second phase of the decanter is directed to a column (22) that separates water as the bottom product and recycles it to the processes, and an upper stream that is fed to a third distiller (23), which produces a flow of

acetone-ethanol as the distillate and a bottom mix of butanol-water to be recycled to the decanter. The acetone-ethanol stream is sent to a fourth column (24), which renders a highly pure acetone distillate (99.94%) and an ethanol solution (92.3%) as bottom product. The S&P configuration employed by the HBE and HBEB routes follows a different path (Kraemer *et al.*, 2011). The first unit of the sequence is a liquid-liquid extraction column (25) where mesitylene, used as a solvent, separates the most plentiful component; water, followed by a column (26) that removes this aqueous solution as the bottom product and directs it to a decanter (27). The decanter works by eliminating the water and recovering the solvent (mesitylene) to recycle it to the extraction column. The top stream of the column (26) is fed to a distillation unit (28) that separates the ABE rich current into a highly concentrated acetone solution (99.97%) as top distillate and a butanol-ethanol bottom stream. The butanol-ethanol current is sent to a third distillation column (29) that produces a highly purified ethanol (99.93%) distillate and high-purity biobutanol (99.96%) at the bottom.

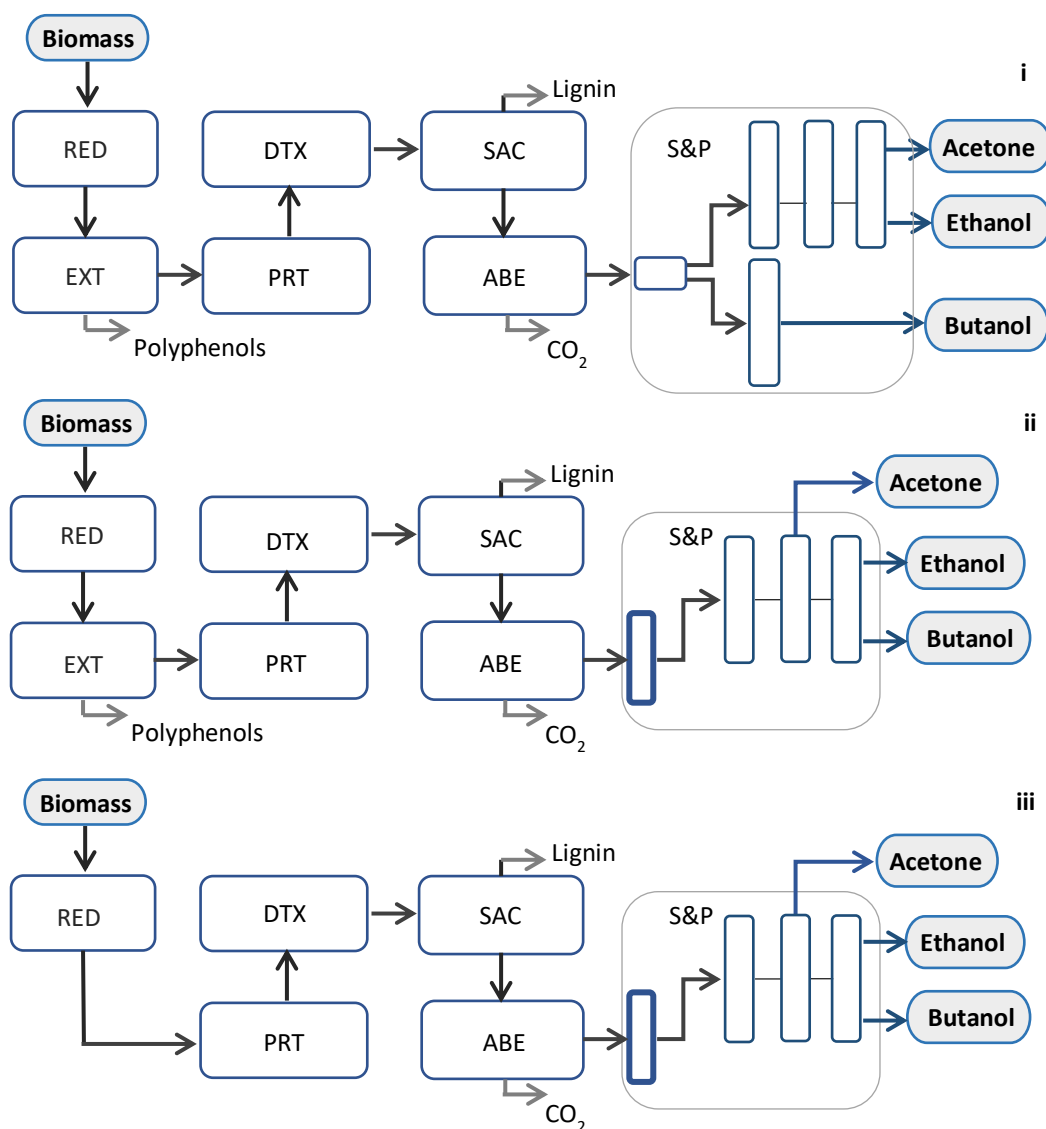


Figure 1. Block diagram for the proposed biorefinery. (i) Biorefining with Conventional Distillation (BCD), (ii) Hybrid Biorefining with Extraction (HBE) and (iii) Hybrid Biorefining without Polyphenol Extraction (HBEB). Based on: Kraemer *et al.*, 2011; Quintero *et al.*, 2013; Jovanović *et al.*, 2017; Patracu *et al.*, 2017 and Kushwaha *et al.*, 2018.

## Operating Assumptions

A conversion rate for each operational reaction was selected as Operating Assumption (OpA). For the best selection of OpAs, we considered the specific performances reported in the literature after sorting out previous works that best fit the present study in terms of biomass feedstocks, technological route, target products, objective, and nature of the experimentations. Table 2 lists all OpAs considered in this study. The process diagrams of the first two conceptual strategies for the biorefinery are shown in Appendix A: i) Biorefining with Conventional Distillation, BCD; and ii) Hybrid Biorefining with Extraction, HBE. The third technological sequence can be figured out from these diagrams.

Table 2. Operating Assumptions considered in process calculations.

Stage	Mechanism	OpA	Model	Reference
EXT	Extractable polyphenols (total concentration as determined in substrate)	5 g/kg DW*	8.8 – 29 g/kg DW 8.6 – 32 g/kg DW 7.5 – 11 g/Kg DW	Sultana <i>et al.</i> , 2008 Safdar <i>et al.</i> , 2016 Berndtsson <i>et al.</i> , 2020
PRT	Fermentable polysaccharide extraction	83.3 %	86 % 72.5 %	An <i>et al.</i> , 2017 Liu <i>et al.</i> , 2016
DTX	Conversion of inhibitors (to gypsum)	100 %	99.3 % 90 % --	Dong <i>et al.</i> , 2018 Jönsson & Martín, 2015
SAC	Conversion to glucose	99 %	90-100 %	Kushwaha <i>et al.</i> , 2018
ABE	Saccharides fermentation	30.82 g/L	33 g/L 30 g/L	Kujawska <i>et al.</i> , 2015 Morone & Pandey, 2014

\* DW=dry weight

## Results and Discussion

The mass balance for all three configurations is shown in Appendix B. The percentage yield of the final (ABE) products (%/ton feedstock) is Ac, 2; Et-OH, 0.7; and BUT, 3.9. The simulation-assisted analysis results confirmed what the literature has suggested regarding the synthesis of biobutanol and its purification by conventional means of distillation, where energy consumption is extensive (Morone & Pandey, 2014). In the BCD configuration, the S&P stage consumes more energy than all other stages combined, at 56% of total consumption. The thermal load for this productive configuration is high due to the steam demands in the separation of the final products. (Figure 2a). It was found that by implementing a hybridization of this method with an alternative configuration for the S&P stage, operating with a pre-extraction column before the final product purification, the energy consumption dramatically decreases (by 56%) with a corresponding decline in demand for cooling operations (Figure 2b). This decrease results from the removal of the high-water content in the ABE broth, carried out in the extraction column assisted by the solvent (mesitylene), which in turn brings forth a decrease in the operational thermal load of the distillation columns further ahead in the process. Our results support the reported trend that traditional biobutanol separation by conventional distillation makes biobutanol production more expensive than bioethanol. Product separation and purification of the ABE broth in biobutanol synthesis is a greater critical challenge than it is in bioethanol production. In bioethanol production, the typical concentration of ethanol in the fermentation broth is 7-10% (w/w), which allows for a simpler separation. It has been reported that the most energy-demanding stage in bioethanol synthesis is detoxification (Quintero *et al.*, 2013). On the other hand, biobutanol ABE fermentation liquors are more complex and generally yield smaller titers (< 2% (w/w) in our simulation), therefore the greater complexity in purification. Our results stress the fact that implementing alternative strategies for the S&P stage in biobutanol production is key to making this biofuel competitive, as suggested in previous works (Bankar *et al.*, 2013; Nanda *et al.*, 2014; Bušić *et al.*, 2018; Kushwaha *et al.*, 2018; Guo *et al.*, 2022).

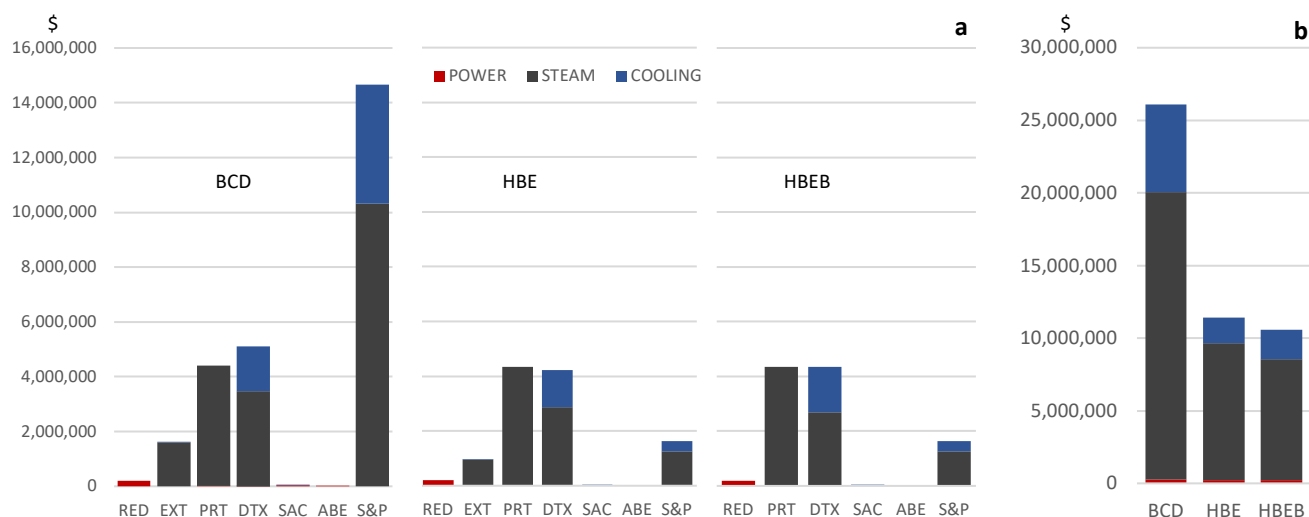


Figure 2. (a) Energy cost by stage, three configurations (BCD, HBE & HBEB), (b) comparative energy cost.

For all three technological routes, Operating Costs (OC) confirm energy demands (UTL) as the highest of all costs (at 76.85%, 64.21% and 61.68% respectively to BCD, HBE, HBEB), followed by raw materials (RM), facility dependent costs (FD), cultures (CL), labor costs (LR) and laboratory expenses (LAB) (Figure 3). Since steam and cooling make up to 99.95% of energy demands (UTL), our results are consistent with the assertion made by authors in the field, who have reported that biorefineries are energy-intensive systems with high steam and heat requirements, so a common hotspot for biorefining processes is energy consumption (Bello *et al.*, 2019; Pugazhendhi *et al.*, 2019; Liu *et al.*, 2022). In percentage terms, the total revenue (TR) of the biorefinery is composed of a), averaged for the BCD and HBE configurations: BUT (39.8%), CO<sub>2</sub> (27.9%), polyphenols (13.2%), Ac (10.5%), lignin (6.3%), and Et-OH (2.2%), while b), for the HBEB route: BUT (45.9%), CO<sub>2</sub> (32.2%), Ac (12.1%), lignin (7.3%), and Et-OH (2.5%) (Figure 4).

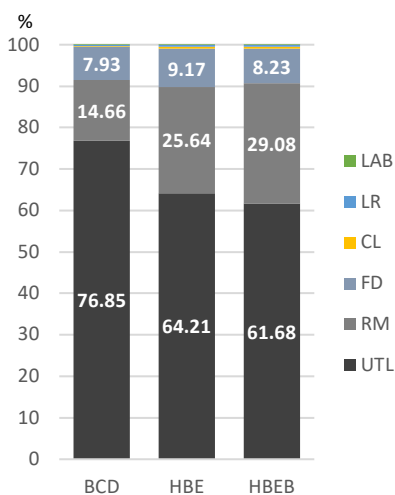


Figure 3. Operation Costs, percent distribution (OC %)

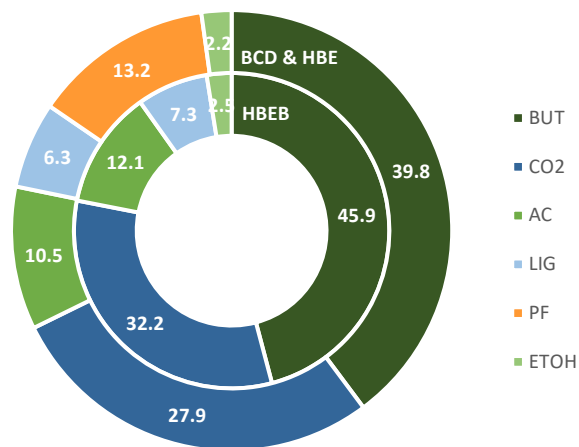


Figure 4. Total Revenue, average percent distribution (TR, %)

It was found that for the BCD configuration, Net Operating Costs (NOC) exceed 4.2 times the Total Revenues (TR) for a processing capacity of 100 ton/day of the substrate, with a downward trend correlation to increases in plant capacity, resulting in 3.4 and 3.3 for 500 and 1,000 ton/day respectively. Likewise, the results showed an NOC/TR ratio of 2.4, 1.99 and 1.8; and 2.1, 1.77, and 1.74 corresponding to the HBE and HBEB strategies and biomass processing capacities of 100, 500 and 1,000 tons per day. On average, the reduction in Total Capital Investment (TCI) from BCD to HBE and HBEB alternatives was 35.1% and 48.9%, which represents a drastic abatement in capital requirements (Figure 5). A simulation of production increases for each plant capacity and all three production routes showed a reduction trend in the Unit Production Cost (UPC) of biobutanol for increases in the tonnage produced annually (due to greater use of all

installed resources). The highest rates of productivity for each case generated a UPC of 28.2, 22.96 and 22.21 \$/kg of butanol for the BCD route; while the HBE path performs at 13.94, 11.67 and 10.51 \$/kg and HBEB processes result in 11.99, 10.07 and 9.88 \$/kg of biobutanol produced (Figure 6).

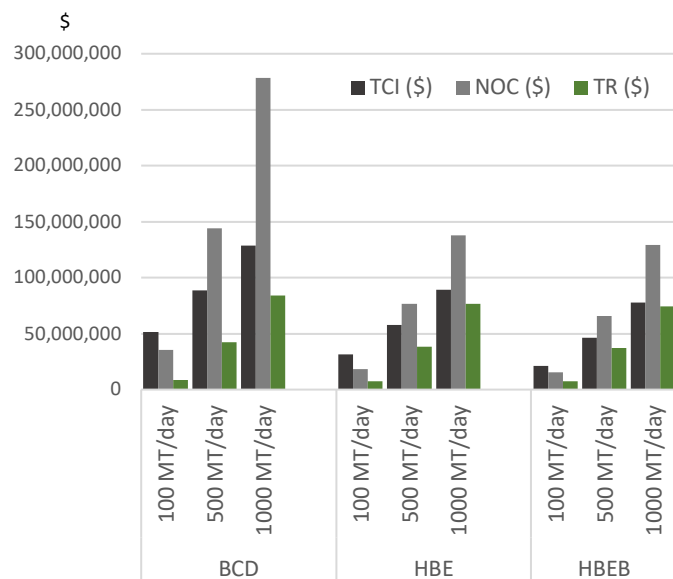


Figure 5. Economic performance of biorefinery BCD, HBE & HBEB configurations

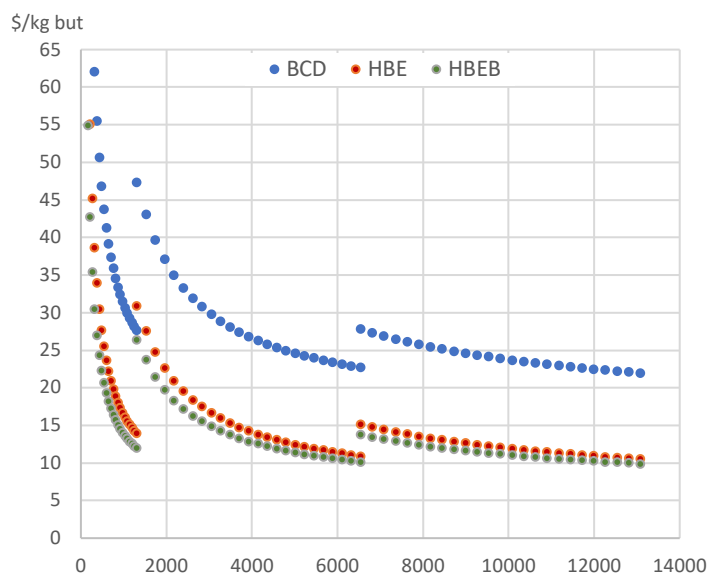


Figure 6. Unit Production Cost per kg of biobutanol produced (UPC)

The results of this evaluation suggest that the best scenario for the synthesis of biobutanol from broccoli residues comes with a technological alternative “HBEB” type, in terms of both, TCI and UPC of butanol. However, for all scenarios and plant capacities, Gross Margin and Return of Investment (ROI) have a negative value, while payback time and the Internal Rate of Return (IRR) are non-existent due to the negative financial and economic performance of the project. Appendix C lists a summary of equipment units, specifications, and purchase costs, as well as the executive summary for the economic evaluation of all technological configurations for a production plant capacity of 100 ton/day.

Our study shows that the concept of biorefinery we proposed is economically unfeasible due to the high NOC. Our best results give a TCI of 129 million USD (MM\$) for 1000 ton of broccoli residues processed per day and place the biofuel cost at 9.88 \$/kg, which would call for a minimum selling price (MSP) of 10 \$. Several publications can be found in the literature dealing with the techno-economic analysis of biorefineries for butanol production based on ABE fermentation and different configurations. Although all studies differ in terms of design, operating conditions, feedstock prices, yield, assumptions, feedstock and carbohydrate availability, a few of them could provide an appropriate basis for comparison with this work. A virtual plant that processes 12,000 ton of sugar cane a day in Brazil gives a TCI of 314 MM\$ and MSP of 1.1 \$/kg of biobutanol (Pereira *et al.*, 2015). A design (without pretreatment stage) processing from 100 to 2000 ton/day of wheat straw in Mexico offers a TCI from 22 to 187 MM\$ and UPC from 2.59 to 1.37 \$/L (Sanchez *et al.*, 2017). A plant processing wheat straw at 3000 ton/day results in TCI of 440 MM\$ and, despite achieving a MSP of 1.3 \$/L, it was deemed minimally viable (Haigh *et al.*, 2018). A simulation of large-scale manufacturing of biobutanol from corn stover in the US concludes that the production of this biofuel can be economically feasible depending on certain circumstances. This study was based on feedstock value chains making numerous assumptions. With a plant capacity of 2,211 ton/day and TCI of 337 MM\$, the results produce a gross disparity in MSP, ranging from 1.22 \$/L to 10.73 \$/L (Alavijeh & Karimi, 2019). A simulated biorefinery processing 7,700 ton/day of cassava in Colombia resulted in TCI of 243 MM\$ and MSP of 1.4 \$/L, with a reported financial breakeven point at 7,500 ton/day of feed flow (Meramo *et al.*, 2021). A biorefinery processing 2,200 ton/day of wheat straw results in a UPC of 0.98 \$/kg and a TCI of 431 MM\$ (Molina-Guerrero *et al.*, 2021), and a conceptual biorefinery to produce biobutanol from apple pomace with a capacity of 125-500 ton/day gives a TCI of 53-343.6 MM\$ and UPC of 0.71-5.38 \$/kg (Molina-Guerrero *et al.*, 2022). Although the benefits of simulation techniques could enable high-capacity plants to achieve commercial-scale, in practicality large production may prove unrealistic, since it is subject to the challenges associated with raw materials availability

and the related efficiency of their value chains. Making a conciliatory effort and broad considerations, all these works seem to convey a level of uncertainty, and our work would appear to be well-grounded and within logical limits.

A thriving economy that includes increasing reliance on biological processes and bio-based products is a key element in the overall global sustainability transition. The global shift of transportation fuels from oil-based carburants to fuels derived from renewable resources and worldwide demand for clean and environmentally friendly energies demand a world-scale paradigm shift. Second generation biofuels need more time, research, better technologies, and a clear policy framework to develop before they can reach the energy markets and have a real impact on the economy. Biobutanol production from lignocellulosic residues is not yet viable; the reduction in processing costs is required to increase its profitability, making its production commercially viable. For successful biobutanol commercialization, numerous aspects should be considered, for example, the regional value chains of the biomasses used as primary feedstocks. As far as we know, there are no previous studies dealing with the biorefining of broccoli residues, whose availability in the state of Guanajuato is abundant. The significant amounts of agricultural residues of this vegetable generated in this Mexican province can positively contribute to the national economy once the technologies required for its biotransformation to biobutanol and other fuels and products are fully developed.

Simulation modeling is a breakthrough in computer science and engineering that enables the design, planning, and testing of proposed methodologies for large-scale industrial processes without incurring the huge and risky costs of pilot production without prior knowledge of the technicalities. Our results show the relevance of the analysis of possible productive scenarios to transform and revalue the large amounts of broccoli residues generated in Guanajuato for biobutanol synthesis and integrating its biorefining in the regional agro-industrial and economic panorama. Our work outlines the significance of computer-aided simulation in the design of strategic methodologies in the valorization of residual biomass for the advancement of global, national and regional energy objectives. The findings of this work suggest that progress can be made in the arena of broccoli residue conversion for biobutanol production, by implementing new production strategies in addition to new technological methods and biochemical routes along the process path and performing technoeconomic analysis assisted by simulation.

This study has two main limitations. First, although the biochemical composition of broccoli has been addressed by various studies and researchers, a true conciliation of criteria is needed to achieve a definite or, at least, a better understanding of the compositional matrix of this important vegetable. We have proposed a biochemical matrix based on different studies that agree to a considerable degree, as well as by comparing the chemical composition proposed by different authors for other similar species. Second, the lack of previous studies in the field of broccoli biorefining may lead to some inaccuracy in our calculations and process parameters.

## Conclusions

In the current biorefining industries, it has become critical to develop innovative models for the efficient and economic purification of the final products. The nature of the mixture obtained as the fermentation broth requires technological strategies that can considerably reduce the energy demands for its separation. The obtained results confirmed that the synthesis of biobutanol offers a wide opportunity window for the design and innovation in purification processes, which may integrate strategies that potentially simplify the thermal dynamics of distillation units and operations, since their combined energy requirements are large and thus, greatly limit the economic efficiency. However, it is also important to consider the heat demands in the operations of pretreatment (PRT) and detoxification (DTX), which are extensive by their own. The operative strategy proposed for the final separation and purification of ABE products, which integrates an extraction unit as a palliative step for the extensive thermal demands, offers an abbreviated dynamism for the final distillation operations, bringing forth lower operating costs. This option, introduced in the two technological routes: HBE and HBEB, enables superlative financial performances and is conducive to important reductions in terms of Total Capital Investment (TCI); among these, the HBEB strategy yields the best results regarding biobutanol production, UPC (\$/kg of biobutanol produced) and purity of all ABE products. In biorefining, the integration of commercially profitable side-stream byproducts and metabolites into the organization portfolio significantly contributes to the total revenue (TR) of the plant, bringing it closer to economic viability. This being the case for the present development, yet the global process to produce biobutanol from the mentioned agricultural substrate falls short of rendering a positive financial outcome to the designed biorefinery. This work highlighted the immense opportunity implicit for R&D&I in the arena of separation and purification methods in the biorefining of lignocellulosic biomass to produce renewable second-

generation liquid biobutanol, and for the recovery of valuable byproducts like CO<sub>2</sub>, a bioindustrial feedstock with much relevance in sustainability, lignin, a promising chemical intermediate, and potential fuel, and the highly appreciated polyphenolic compounds, which are widely used in health and nutrition, helping to envisage a bright future for the biorefining industries in light of the incoming biocircular economy. Finally, our research revealed that the use of specific renewable resources generated as waste in the state of Guanajuato can become important energy resources for transportation once the appropriate technologies and value chains have been properly implemented. On this basis, future research should focus on the rigorous examination of broccoli residues and laboratory-scale processes for their transformation to biobutanol, as well as for the recovery of their polyphenols and other extractable metabolites.

**Acknowledgments and Funding:** We acknowledge financial support from Universidad de Guanajuato DIQEB Department -Science and Engineering Division and Dirección de Apoyo a la Investigación y al Posgrado (Convocatoria Institucional de Investigación Científica 2021) project (054/2021).

**Author contributions:** L.G.F.-T.: investigation, writing—original draft, design, analysis and interpretation of data; E.V.-N.: editing; C.E.M.-G.: conceptualization, supervision, review and editing, funding, project administration.

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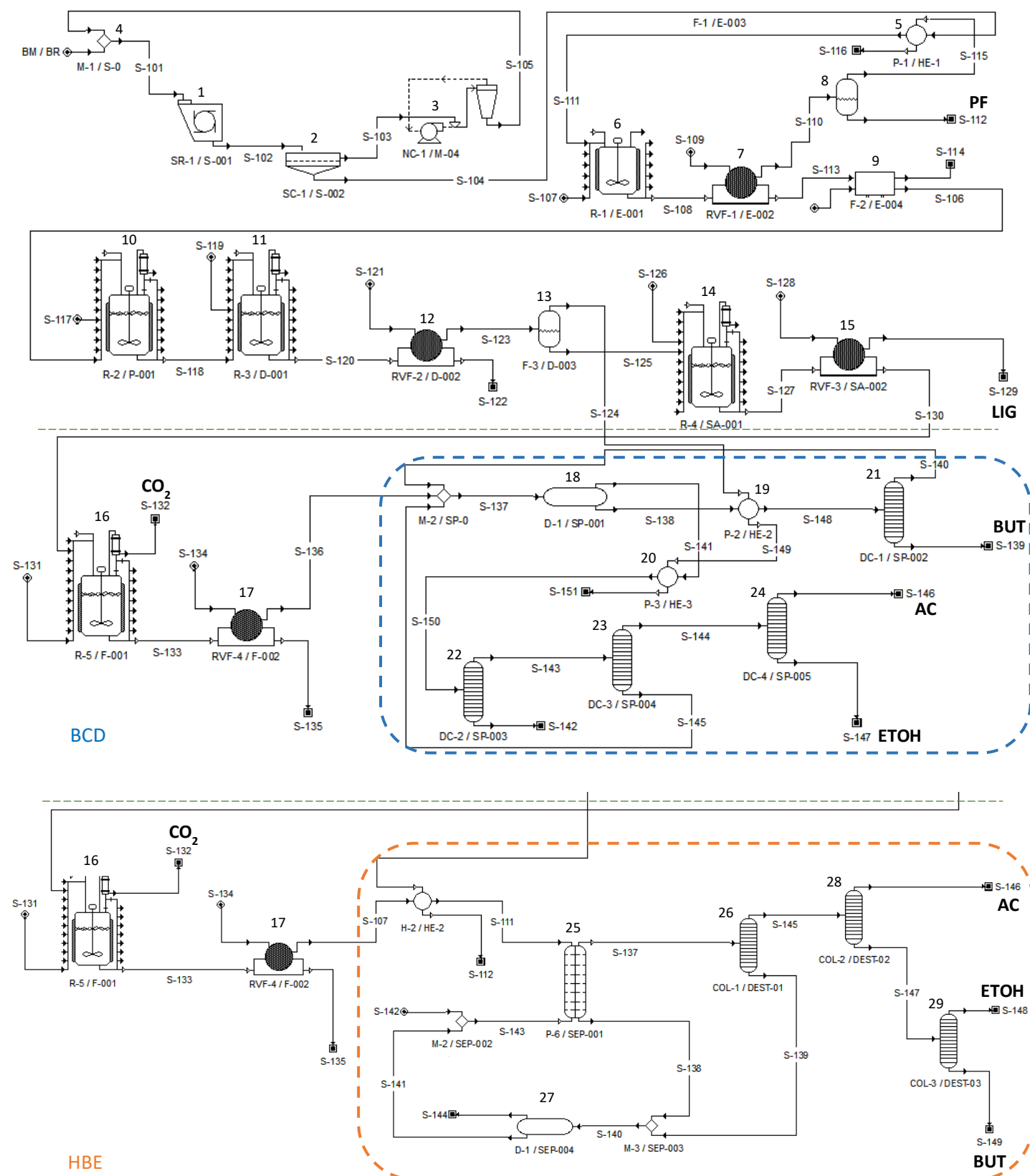
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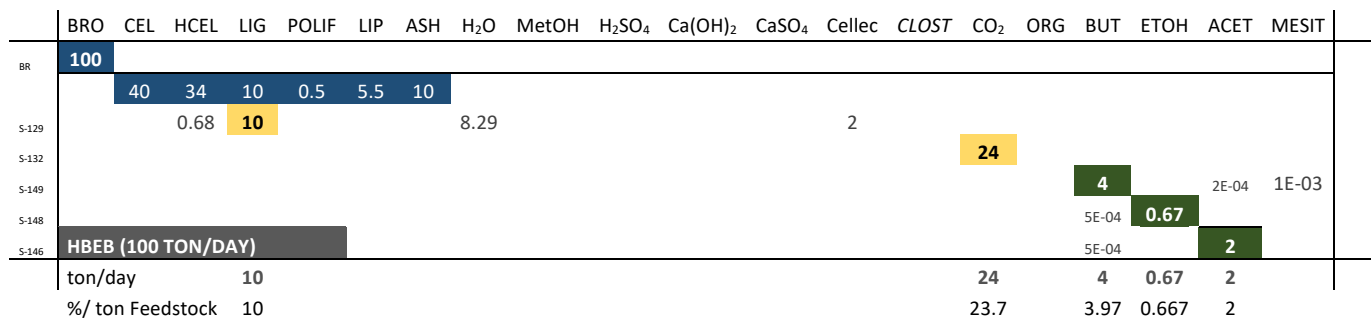
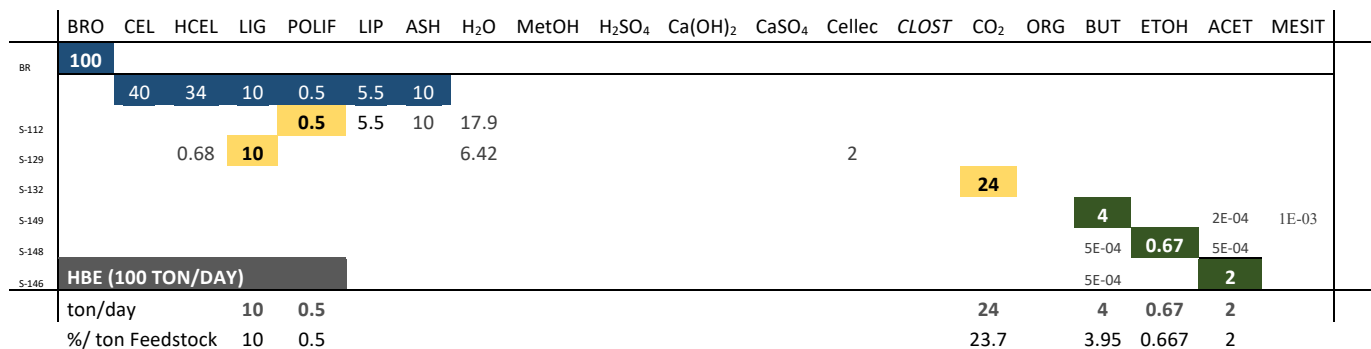
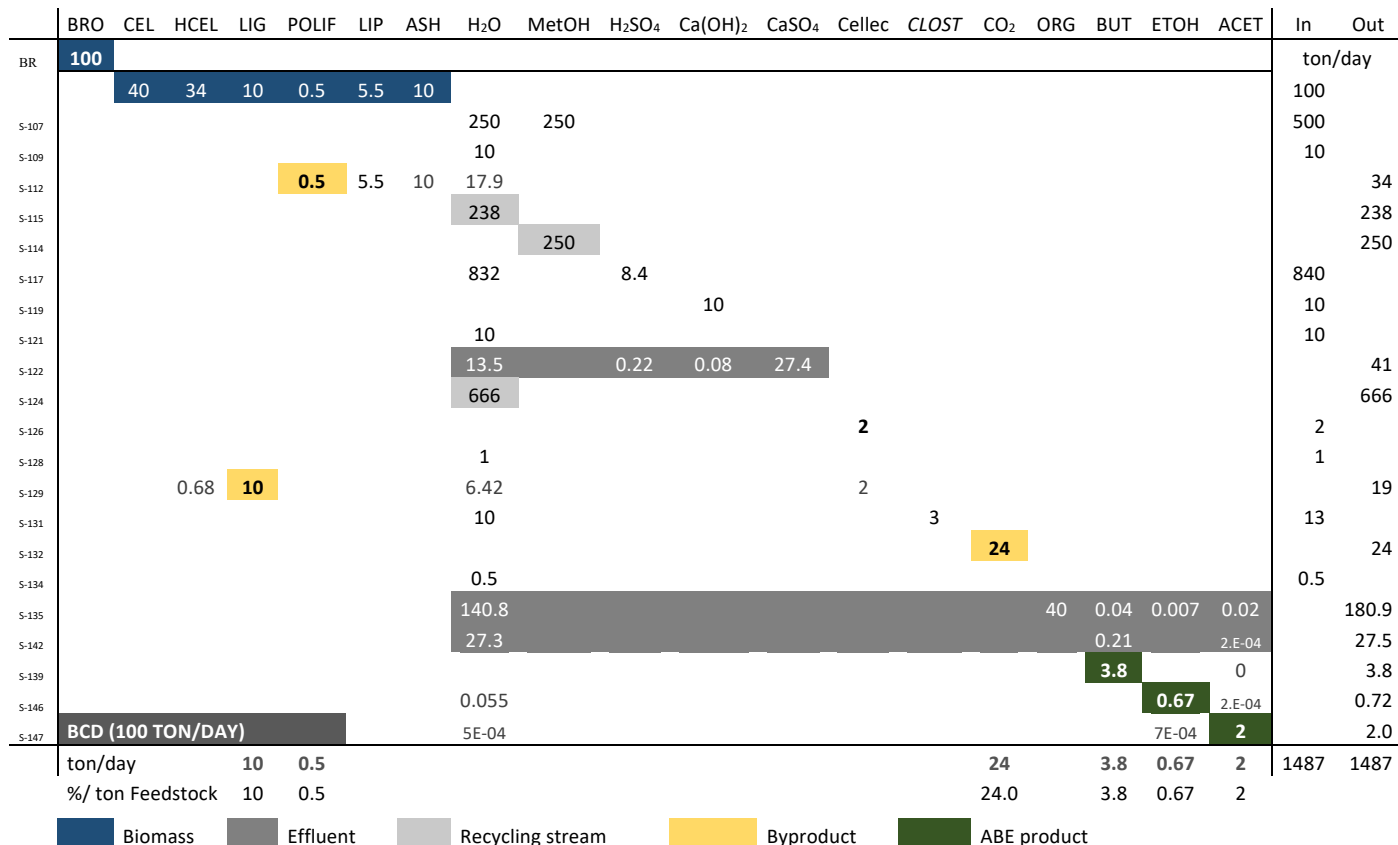
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### Supplementary Material

Appendix A. Process diagram, configurations BCD and HBE and, the two S&P operating approaches.



Appendix B. Global mass balance.



## Appendix C. Summary: equipment list and purchase costs; Economic evaluation executive summary

Stage	Equipment	U	Capacity	U Cost (\$)	Cost (\$)	U	Capacity	U Cost (\$)	Cost (\$)	U	Capacity	U Cost (\$)	Cost (\$)
RED	S-001 Shredder	2	2,104 kg/h	34,000	68,000	2	2,102 kg/h	34,000	68,000	2	2,104 kg/h	34,000	68,000
	S-002 V. Screen	2	2,104 kg/h	3,000	6,000	2	2,102 kg/h	3,000	6,000	2	2,104 kg/h	3,000	6,000
	M-04 Pneumatic C	1	150 m	43,000	43,000	1	150 m	43,000	43,000	1	150 m	43,000	43,000
	HE-1 Heat Exch	1	3.55 m2	17,000	17,000	1	3.72 m2	18,000	18,000	1	5.01 m2	21,000	21,000
EXT	E-001 Blending tank	5	350 m3	257,000	1,285,000	5	348 m3	256,000	1,280,000				
	E-002 R Vac Filter	1	15.19 m2	33,000	33,000	1	15.17 m2	33,000	33,000				
	E-003 Flash Drum	1	205.36 L	1,000	1,000	1	205.12 L	1,000	1,000				
	E-004 Rotary Dryer	1	628.04 L	2,000	2,000	1	62.31 L	2,000	2,000				
PRT	P-001 Stirred Reactor	1	150.82 m3	481,000	481,000	1	150.64 m3	480,000	480,000	1	151.93 m3	482,000	482,000
DTX	D-001 Stirred Reactor	1	23 m3	135,000	135,000	1	22 m3	135,000	135,000	1	34 m3	143,000	143,000
	D-002 R Vac Filter	1	3.97 m2	19,000	19,000	1	3.99 m2	19,000	19,000	1	5.70 m2	22,000	22,000
	D-003 Flash Drum	1	1,724 L	4,000	4,000	1	1,722.4 L	4,000	4,000	1	1,719.4 L	4,000	4,000
SAC	SA-001 Stirred Reactor	3	260 m3	406,000	1,218,000	2	260 m3	406,000	812,000	2	260 m3	406,000	812,000
	SA-002 R Vac Filter	1	36.15 m2	46,000	46,000	1	36.11 m2	46,000	46,000	1	36.04 m2	46,000	46,000
ABE	F-001 Stirred Reactor	5	400 m3	502,000	2,510,000	2	200 m3	368,000	736,000	2	200 m3	368,000	736,000
	F-002 R Vac Filter	1	30.42 m2	29,000	29,000	1	30.38 m2	29,000	29,000	1	30.32 m2	29,000	29,000
S&P	SP-001 Decanter	1	36154 L	87,000	87,000								
	HE-2 Heat Exch	1	9.5 m2	31,000	31,000	1	1.3 m2	10,000	10,000	1	1.3 m2	10,000	10,000
	HE-3 Heat Exch	1	.52 m2	8,000	8,000								
	SP-002 Distillation	8	17,380 L	25,000	200,000								
	SP-003 Distillation	1	1,466,36	15,000	15,000								
	SP-004 Distillation	1	241,21 L	11,000	11,000								
	SP-005 Distillation	1	201.82 L	21,000	21,000								
	SEP-001 Diff. extractor					1	4,390 L	44,000	44,000	1	4,380 L	44,000	44,000
	SEP-004 Decanter					1	1.78 L	7,000	7,000	1	1.78 L	7,000	7,000
	Dest-01 Distillation					1	487.89 L	14,000	14,000	1	488.45 L	14,000	14,000
	Dest-02 Distillation					1	98.14 L	9,000	9,000	1	98.25 L	9,000	9,000
	Dest-03 Distillation					1	61.8 L	13,000	13,000	1	61.88 L	13,000	13,000
	Other				1,567,000				952,000				627,000
					7,837,000				4,761,000				3,136,000

Plant capacity: 100 ton/day	BCD	HBE	HBEB	
Total Capital Investment	51,629,000	31,250,000	21,052,000	\$
Capital Investment Charged to This Project	51,629,000	31,250,000	21,052,000	\$
Operating Cost	40,449,000	22,380,000	19,655,000	\$/yr
Credits	5,082,122	4,162,665	3,955,343	\$/yr
Net Operating Cost	35,367,062	18,217,260	15,699,261	\$/yr
Revenues	3,360,000	3,501,000	3,505,000	\$/yr
Total Revenues	8,442,122	7,663,665	7,460,343	\$/yr
Cost Basis Annual Rate	1,254	1,307	1,309	MT MP/yr
Unit Production Cost	32,253.23	17,121.35	15,018.98	\$/MT MP
Net Unit Production Cost	28,200.87	13,936.78	11,996.52	\$/MT MP
Unit Production Revenue	2,679.57	2,678.36	2,678.36	\$/MT MP
Gross Margin	-	-	-	
Return On Investment	-	-	-	
Payback Time N/A	N/A	N/A	N/A	
IRR (After Taxes) N/A	N/A	N/A	N/A	
NPV (at 7.0% Interest)	-	-	-	