A Superstructure-Based Lignin Valorization Process Optimization Model for Lignocellulosic Biorefineries through Biological Upgrading

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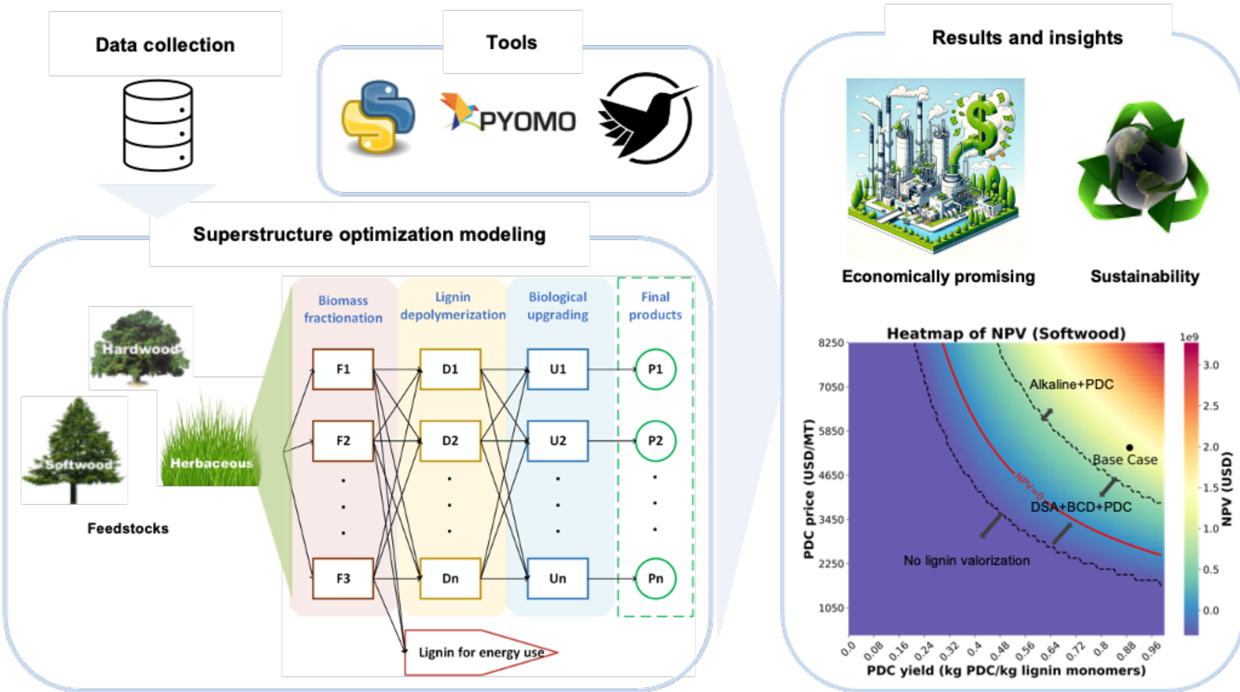
ABSTRACT

This study presents an optimization framework to identify economically viable pathways for lignin valorization in biorefineries that employ biological upgrading. The economic potential for converting lignin from softwood, hardwood, and herbaceous plants into valuable bioproducts is evaluated. The research indicates that the production of 2-pyrone-4,6-dicarboxylic acid (PDC) from softwood is the most economically promising, with an estimated net present value (NPV) of $1,259 million and an internal rate of return (IRR) of 25.63%. Capital costs represent a significant portion of the total expenses across all scenarios. Revenue from woody feedstocks is largely derived from lignin-based products, while for herbaceous plants, co-products such as sugars are the main revenue contributors. The financial viability is influenced by factors such as the price and yield of the final products, the cost of feedstocks, and the capital expenses. The analysis provides strategic insights for the development of lignin valorization biorefineries and guides the chemical industry toward a more sustainable use of renewable carbon sources.

KEYWORDS: Lignin, Fermentation, Biorefinery, Mixed-Integer Non-Linear Programing, Process System Engineering

Abstract Graphic



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Synopsis

Our paper introduces an optimized model for lignin valorization in biorefineries, enhancing sustainable chemical engineering through biological methods.

1. Introduction

As the urgent need to reduce CO_2 emissions intensifies, shifting from fossil feedstocks to renewable lignocellulosic resources (such as agricultural residues, wood, and herbaceous biomass) presents a promising and forward-thinking solution. Lignocellulosic materials, being the world's most plentiful renewable terrestrial resource, hold the potential to partially replace fossil feedstocks in the production of energy and chemicals.[1]

Lignocellulosic biomass primarily consists of cellulose, hemicellulose, and lignin, with lignin accounting for 15 to 40% of the biomass's dry weight.[2,3] As the sole aromatic polymer in biomass, lignin's market size was valued at $970.7 million in 2020 and is projected to reach $1.12 billion by 2027.[4] Despite its potential, lignin is often viewed as a low-value byproduct, typically burned for power generation in industrial processes such as pulping and papermaking.[5] Commercial biorefinery processes that convert lignin into high-value products are scarce, primarily due to the technical challenges involved in lignin valorization.[6]

However, lignin is a polymer rich in aromatic monomers which may offer significant potential for producing biochemicals that can replace fossil fuel-derived chemicals. By harnessing lignin more effectively, we can help mitigate climate change and foster circular and net-zero bioeconomies.[7] Consequently, numerous efforts are focused on developing innovative techniques to transform lignin into value-added products through lignin valorization processes. Usually, a lignin valorization process consists of three distinct stages: (1) biomass fractionation, (2) lignin depolymerization, and (3) upgrading to bioproducts.[8]

In particular, the biological upgrading of lignin represents a promising valorization approach, as microbes can convert aromatic lignin monomers into single compounds via biological funneling.[9] This method is environmentally friendly and operates under milder conditions compared to chemical or thermochemical methods, which often require harsh chemicals, high temperatures, and high pressures. As a result, biological upgrading may lead to lower energy consumption. Furthermore, the enzymes and microorganisms employed in this process can be highly specific and selective, targeting particular bonds or functional groups in lignin. This selectivity enables the production of targeted compounds with minimal byproducts, thereby improving the overall efficiency and value of the process.[9] For example, Linger et al. used the ligninolytic bacterium *Pseudomonas putida* to generate polyhydroxyalkanoates (PHA) from lignin as a carbon source.[10] Kosa and Ragauskas[11] effectively employed *Rhodococcus opacus* DSM1069 and PD630 strains to transform ethanol organosolv lignin into lipids.[11] The lipids produced through this process can subsequently be converted into biodiesel, a renewable source of energy. Becker et al. employed metabolic engineering to optimize the metabolic pathway of *Corynebacterium glutamicum*, enabling the production of cis,cis-muconic acid from lignin-derived compounds such as benzoic acid, catechol, and phenol.[12] Cis, cis-muconic acid is a platform for the production of adipic acid, which in turn is a precursor for the production of polymers such as nylon.[13] Perez et al. engineered the bacterium *Novosphingobium aromaticivorans* DSM12444, to transform aromatic compounds from lignin into 2-pyrone-4,6-dicarboxylic acid (PDC). PDC holds potential as a precursor for polyester.[14]

As a variety of lignin valorization techniques emerge, a key challenge lies in providing stakeholders with a systematic comparison and analysis to identify economically viable pathways and bioproducts derived from lignin. Researchers and biorefinery practitioners require tools for selecting the most profitable feedstocks, processes, and end products derived from lignin. Thus, recent studies have explored the system-level optimization of lignin valorization. Huang et al. employed superstructure optimization to evaluate the economic impact of lignin valorization within the context of lignocellulosic biorefineries, to identify the types of corn stover pretreatments that could render lignin valorization economically attractive. However, the study treated lignin valorization as a single block in the superstructure, without specifying the details about the technological alternatives.[15] Giuliano et al. and Josefina Robinson et al. developed integrated superstructure-based optimization models to evaluate the conversion of lignin into biobased products.[16] In each of these studies, techno-economic models were integrated with optimization models, and mixed-integer linear/nonlinear programming (MILP/MINLP) models were employed for optimization purposes, offering valuable insights into the lignin valorization research. However, they neither specifically addressed the biological upgrading of lignin nor utilized various feedstocks to derive lignin and compare the performance of these different feedstocks. Furthermore, the lignin valorization stages (i.e., pretreatment, depolymerization, and upgrading) were not explicitly considered which may limit the ability to provide insights into the cost drivers of the process.

Another considerable challenge in the system analysis of lignin valorization processes stems from data collection and code implementation for optimization. Obtaining the necessary data can be difficult, as it often remains unavailable. Characterizing data for each process alternative calls for comprehensive information, encompassing process reactions, process yield, chemical and utility usage, equipment costs, and product prices. As many lignin valorization processes are still in development, limited process and economic data is accessible.

To this end, the goal of this paper is to develop a comprehensive process superstructure optimization model of lignin valorization biorefinery with biological upgrading. We aim to identify the required conditions necessary to render biological lignin upgrading profitable. We consider various types of feedstocks (hardwood, softwood, and herbaceous plants) representative of the broad spectrum of lignocellulosic materials, and collect data from various sources, including published literature and national lab reports, to ensure a well-informed and accurate model. In addition, we compare alternative processes for each step in the lignin valorization biorefinery. Our work constitutes the first systematic analysis of lignin valorization using biological upgrading pathways and provides relevant insights into the main economic drivers of this process.[17,18]

2. Superstructure construction

The proposed process superstructure is presented in Figure 1. We capture all desired alternatives, including types of feedstocks, conversion processes in each stage, and potential final bioproducts from lignin valorization through biological upgrading, based on an extensive literature review.

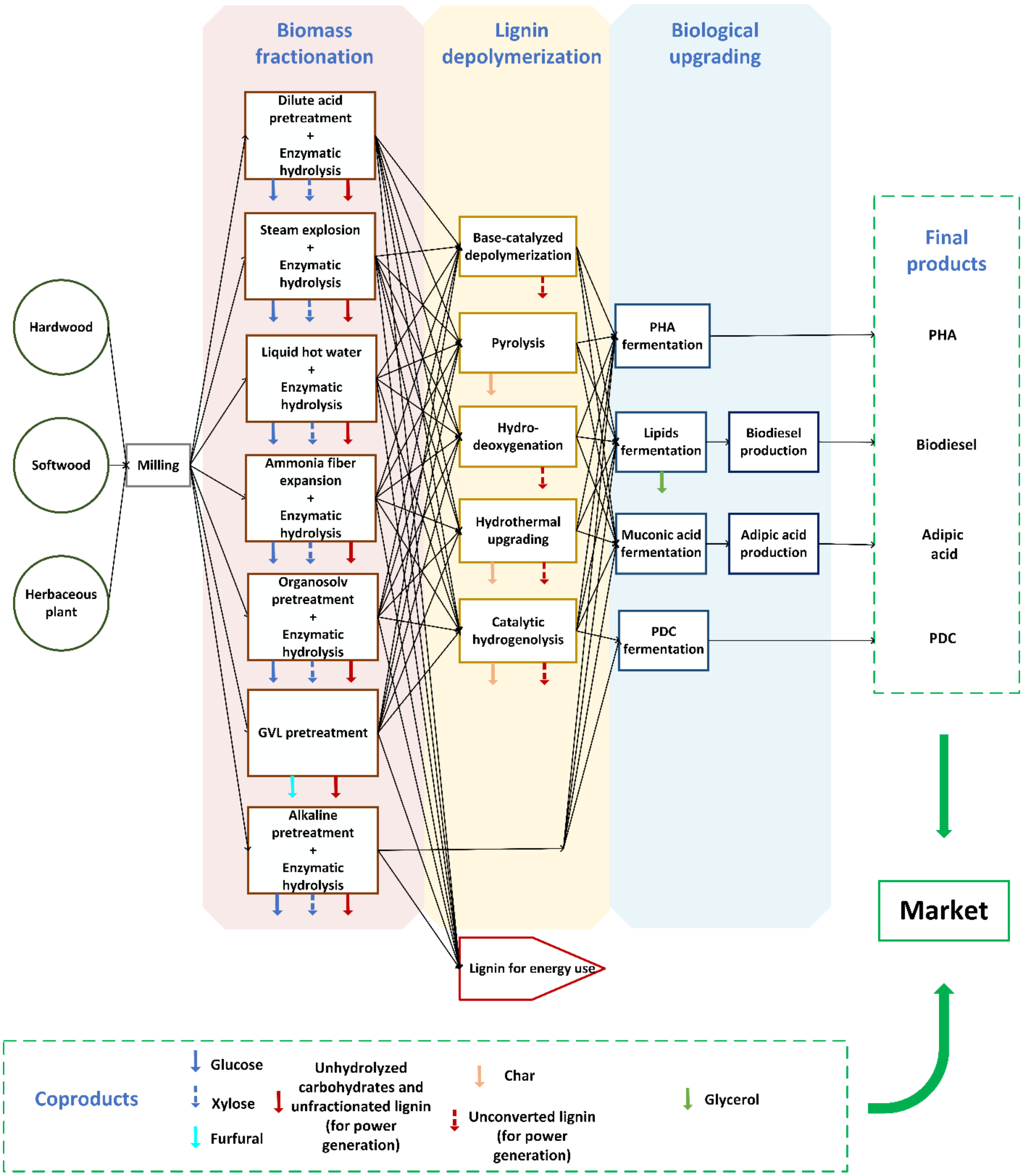

Figure 1. Process superstructure of a lignin valorization biorefinery system with biological upgrading, detailing the conversion processes for hardwood, softwood, and herbaceous biomass. Milled biomass undergoes fractionation into a lignin fraction and coproducts. The lignin fraction is depolymerized, followed by biological upgrading, culminating in the synthesis of marketable

bioproducts. Each process step generates associated coproducts. Alternatively, the lignin fraction can be combusted for energy.

The superstructure encompasses three process stages, (1) biomass fractionation, (2) lignin depolymerization, and (3) biological upgrading. Each stage comprises alternative processes, which are discussed in more detail in the **Supporting Information**. Table S1 in **Supporting Information** outlines specific operating conditions for each corresponding process, while Table S2 in **Supporting Information** illustrates the process yields associated with each process.

2.1 Biomass fractionation

The goal of biomass fractionation (commonly referred to as pretreatment) is to extract the carbohydrate fraction (cellulose and hemicellulose) and remove lignin from lignocellulose.[17] In traditional biorefineries, a stream consisting of lignin-rich residues is obtained at the end. This stream is generally considered as a low-cost energy source or low-value by-product. In this study, lignin is considered a valuable feedstock that can be used to produce fuels and chemicals. Biomass fractionation typically employs a combination of physical, chemical, or thermochemical techniques.[18] The alternative biomass fractionation methods examined in this study include dilute acid pretreatment, steam explosion, liquid hot water, organosolv pretreatment, ammonia fiber expansion, gamma-valerolactone (GVL) pretreatment, and alkaline pretreatment (Figure 1, Table S1).

In the proposed superstructure, enzymatic hydrolysis is integrated into the biomass fractionation stage (except for GVL pretreatment) to convert cellulose and hemicellulose into glucose and xylose (we assume that hemicellulose composition can be well represented by xylose), respectively. The GVL pretreatment incorporates a high-temperature phase that breaks down cellulose into glucose and hemicellulose into furfural, thus eliminating the requirement for enzymatic hydrolysis.[19] The lignin fraction is then processed in the next stage for further conversion. We assume that the quality of lignin obtained from different feedstocks and after various fractionation processes is equivalent.

Glucose extracted from cellulose, along with xylose and furfural obtained from hemicellulose, are treated as marketable byproducts that contribute to revenue generation at this stage and are valued based on the minimum selling price from the National Renewable Energy Laboratory (NREL) reports and Baral et al.[20,21] Unhydrolyzed carbohydrates and unfractionated lignin are routed to the boiler and turbogenerator to produce electricity (Figure 1).

We explore three distinct types of feedstocks: hardwood, softwood, and herbaceous plants, differentiated by their unique composition of cellulose, hemicellulose, and lignin (Table S3). Hardwood, obtained from deciduous trees such as oak, maple, and birch, typically exhibits a high cellulose and lignin content, but a lower hemicellulose content compared to softwood. Softwood, derived from coniferous trees such as pine, spruce, and fir, is characterized by a relatively lower cellulose content and higher lignin and hemicellulose content. Herbaceous plants, including grasses, agricultural residues, and energy crops, possess higher cellulose and hemicellulose content and lower lignin content.[2,22,23]

Prior to biomass fractionation, the feedstocks must be milled to achieve the desired particle size to ensure an efficient fractionation process.[24]

2.2 Lignin depolymerization

Lignin's intricate and heterogeneous structure poses a challenge in depolymerization. Methods used generally employ chemical, thermal, or catalytic processes to cleave the chemical bonds linking lignin's phenolic subunits.[25] Our superstructure explores various depolymerization methods to break down lignin into simpler, metabolically accessible monomers, including: base catalyzed depolymerization, pyrolysis, hydrodeoxygenation, hydrothermal upgrading, and catalytic hydrogenolysis (Figure 1, Table S1).

Depending on the depolymerization technology used, coproducts such as char (from pyrolysis) and unconverted lignin can be harnessed for heat and energy production. Char was assumed to be sold in the market, generating additional revenue for the system, while the unconverted lignin was directed to the boiler and turbogenerator for power generation. Furthermore, our superstructure also includes the possibility of sending lignin directly to a boiler and turbogenerator for electricity generation.

2.3 Biological upgrading

Depolymerized lignin can be converted by certain microorganisms into value-added products in fermentation processes. In this study, the final products obtained from the biological upgrading of lignin include: PHA (polyhydroxyalkanoates), biodiesel from lipids, adipic acid from muconic acid, and PDC (2-pyrone-4,6-dicarboxylic acid).

Currently, the biological valorization of lignin is at a low technology readiness level, and the product yields from these methods vary significantly across different experiments, as demonstrated in Figure 2. In the optimization model, we employ the values at the 75% percentile of the gathered yield data, and we later explore the sensitivity of our results to changes in this parameter.

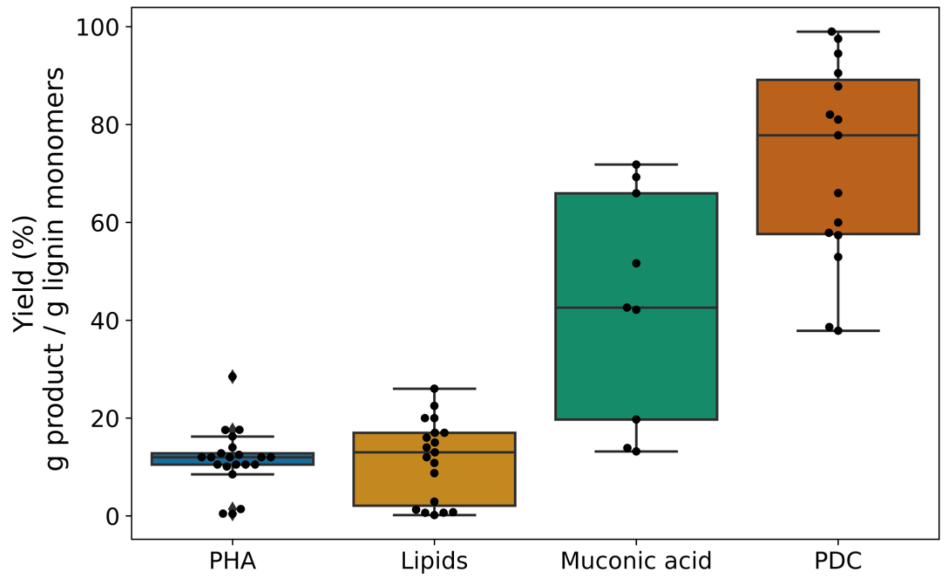

Figure 2. Yield range for PHA[10,26–31], lipids[11,32–37], muconic acid[12,38–42] and PDC[14,19,43–48]

3. Optimization modeling

The lignin valorization superstructure optimization problem is formulated as an MINLP model. An economic objective function is used, along with constraints for mass and energy balances, superstructure connectivity, and economic calculations.

In the model, uppercase characters denote variables; upper case characters in bold are used for sets; and lowercase characters represent parameters. Superscripts are used exclusively for labeling purposes (components (FS: feedstock, PM: polymers, CP: coproducts, UT: utilities, CH: chemicals), and stages ($MILL$: milling, FR: biomass fractionation, DPL: depolymerization, and UPG: upgrading, $BURN$: boiler and turbogenerator, WT: waste treatment)).

3.1 Economic objective function

The economic objective function seeks to maximize the net present value (NPV) of a lignin valorization biorefinery plant (Eq. 1). This approach aims to enhance the plant's profitability and financial sustainability in the near term by choosing the optimal process pathway.

$$NPV = \sum_{t \in \boldsymbol{T}} \frac{CF_t}{(1+r)^t} \tag{1}$$

where CF_t is the cash flow at year t and r is the discount rate. CF_t is defined as:

$$CF_t = (AR - OPEX - FSC)(1 - tax) - f_t CAPEX + tax\ DP_t, \forall t \in \boldsymbol{T} \tag{2}$$

where AR represents the annual revenue, $OPEX$ the annual operating expenses, FSC the feedstock purchasing cost, and $CAPEX$ the initial capital investment. DP_t is the depreciation at year t and f_t is the fraction of capital expenditure spent at year t, where $f_0 = 0.08$, $f_1 = 0.6$, $f_2 = 0.32$, and $f_t = 0$ for other t. Finally, tax is the current tax rate, set as 21%.

3.2 Constraints

3.2.1 Mass and energy balance

Each process (blocks in Figure 1) consists of up to three operations: mixing, reaction, and separation. In each process four types of material flows are considered: feedstock inflow ($F_{c,p}^{IN}$), additional chemicals ($F_{ch,p}^{CH}$), coproducts ($F_{c'',p}^{CP}$), and outflow ($F_{c',p}^{OUT}$). Additionally, we model the supply of utilities (electricity, natural gas, and cooling water) to the system ($U_{ut,p}$).

For the mass balance of each process, the inflow of component $c \in \boldsymbol{C}$ to process $p \in \boldsymbol{P}$ is denoted by $F_{c,p}^{IN}$, and the outflow of component $c' \in \boldsymbol{C}$ from process $p \in \boldsymbol{P}$ is expressed as $F_{c',p}^{OUT}$. The amount of product and coproduct obtained out of each process is given by Eqs. 3 and 4, where $\theta_{c,c',p}^{OUT}$ represents the product/coproduct yield (kg of product $c' \in \boldsymbol{C}$ per kg of feedstock $c \in \boldsymbol{C}$). $\boldsymbol{C}_p^{FEED}$ and $\boldsymbol{C}_p^{PROD}$ represents the subsets of feedstocks and products of process $p \in \boldsymbol{P}$, respectively.

$$F_{c',p}^{OUT} = \sum_{c \in \boldsymbol{C}_p^{FEED}} \theta_{c,c',p}^{OUT} F_{c,p}^{IN}, \forall p \in \boldsymbol{P}, c' \in \boldsymbol{C}_p^{PROD} \tag{3}$$

We estimate the amount of additional chemicals required $F_{ch,p}^{CH}$ in Eq. 4. In this equation, we use the chemical consumption ratio $\mu_{ch,p}^{CH}$ as a parameter, which is defined as the amount in kg of chemical component $ch \in \boldsymbol{CH_p}$, required per kg of inflow.

$$F_{ch,p}^{CH} = \mu_{ch,p}^{CH} \sum_{c \in \boldsymbol{C}_p^{FEED}} F_{c,p}^{IN}, \forall ch \in \boldsymbol{CH}_p,\ p \in \boldsymbol{P} \tag{4}$$

Similarly, the utilities consumption $U_{ut,p}$ in process $p \in \boldsymbol{P}$ is defined by Eq. 5. The utility consumption rate $\mu_{ut,p}^{UT}$ is defined as the amount in kWh of utility $ut \in \boldsymbol{UT}$, that is required per kg of inflow product.

$$U_{ut,p} = \mu_{ut,p}^{UT} \sum_{c \in \boldsymbol{C}_p^{FEED}} F_{c,p}^{IN}, \forall ut \in \boldsymbol{UT},\ p \in \boldsymbol{P} \tag{5}$$

The total inflow of component $c \in \boldsymbol{C}_p^{FEED}$ to process p ($F_{c,p}^{IN}$) is calculated by summing up the incoming flows from all other processes p' (Eq. 6). In this equation, $F_{c,p',p}$ represents the flow of component $c \in \boldsymbol{C}_p^{FEED}$ from process p' to process p. The total outflow of component $c \in \boldsymbol{C}_p^{OUT}$ out of process p ($F_{c,p}^{OUT}$) is calculated by summing up the outflows to all other processes p' (Eq. 7). Finally, Eq. 8 enforces that the inflows toward a process are equal to zero if a process is not selected.

$$F_{c,p}^{IN} = \sum_{p' \in \boldsymbol{P}_p^{IN}} F_{c,p',p}, \forall\ c \in \boldsymbol{C}_p^{FEED},\ p \in \boldsymbol{P} \tag{6}$$

$$F_{c,p}^{OUT} = \sum_{p \in \boldsymbol{P}_{p'}^{OUT}} F_{c,p,p'}, \forall\ c \in \boldsymbol{C}_p^{OUT},\ p \in \boldsymbol{P} \tag{7}$$

$$F_{c,p',p} \leq M * I_p, \forall\ c \in \boldsymbol{C}_p^{FEED},\ p \in \boldsymbol{P}, p' \in \boldsymbol{P}_p^{IN} \tag{8}$$

In the case of biomass milling, the maximum input limit for the biorefinery system is established in Eq. 9.

$$F_{c,p}^{IN} = \sum_{c' \in \boldsymbol{C}^{FS}} I_{c'}^{FS} * q_{max} * \xi_{c',c},\ \ \forall c \in \boldsymbol{C}^{PM}, p \in \boldsymbol{P}^{MILL} \tag{9}$$

where $I_{c'}^{FS}$ is a binary variable determining if feedstock $c' \in \boldsymbol{C}^{FS}$ is selected, while q_{max} signifies the maximum feedstock inflow. The composition of polymer (cellulose, hemicellulose, and lignin) c in feedstock (softwood, hardwood, and herbaceous plant) c' is denoted by $\xi_{c',c}$.

Three components can be sent to the boiler and turbogenerator: (1) the unhydrolyzed cellulose and hemicellulose; (2) the unconverted lignin in the depolymerization stage; and (3) an additionally pathway where, if the lignin is not depolymerized or further upgraded after fractionation, it can be directly routed to the boiler and turbogenerator for power generation. The total amount of electricity produced in this unit is given by Eq. 10, where η represents the efficiency of the boiler and turbogenerator and ρ_c denotes the lower heating value of product c.

$$E_p^{OUT} = \eta \sum_{p' \in \boldsymbol{P}} \sum_{c \in \boldsymbol{C}_p^{FEED}} \rho_c \, x_{p',p} \, F_{c,p'}^{OUT} \, , p \in \boldsymbol{P}^{BURN} \tag{10}$$

3.2.2 Structural constraints

For mutually exclusive processes, only one process can be selected at a time (Eq. 11), we have:

$$\sum_{p \in \boldsymbol{P}_k} I_p = 1, \forall k \in \boldsymbol{K} \tag{11}$$

where $\boldsymbol{K}$ is the set mutually exclusive superstructure stages, which has the following elements: biomass fractionation, lignin depolymerization, or biological upgrading. Finally, the superstructure connectivity is enforced in Eqs. 12 and 13.[49]

$$I_{p'} \leq \sum_{p \in \boldsymbol{P}} x_{p',p} I_p \, , \forall \, p' \in \boldsymbol{P} \tag{12}$$

$$I_p \leq \sum_{p' \in \boldsymbol{P}} x_{p,p'} I_{p'} \, , \forall \, p \in \boldsymbol{P} \tag{13}$$

3.2.3 Economic constraints

The annual revenue (AR) can be derived from the sales of final bioproducts (PHA, lipids, muconic acid, and PDC), coproducts (sugars (glucose, xylose), and furfural, char, unconverted lignin, and glycerol), and electricity:

$$AR = \sum_{p \in \boldsymbol{P}^{UPG}} \sum_{c \in \boldsymbol{C}_p^{UPG}} v_c F_{c,p}^{OUT} + \sum_{p \in \boldsymbol{P}} \sum_{c \in \boldsymbol{C}^{CP}} v_c F_{c,p}^{OUT} + \sum_{p \in \boldsymbol{P}^{BURN}} \nu^E E_p^{OUT} \tag{14}$$

where $F_{c,p}^{OUT}$ represents the outflow of product/coproduct $c \in \boldsymbol{C}^{UPG}$ from upgrading process p, $E_{c,p}^{OUT}$ denotes the electricity generated by boiler and turbogenerator. v_c and ν^E represent the unit prices of final products (for $c \in \boldsymbol{C}_p^{UPG}$), coproducts (for $c \in \boldsymbol{C}^{CP}$), and energy generated from boiler and turbogenerator.

The cost is comprised of annual operating cost ($OPEX$) and the feedstock purchasing cost (FSC). $OPEX$ includes utility cost, additional chemicals cost, waste treatment cost (C^{WT}), and fixed operating cost (FOC). $OPEX$, FSC, and C^{WT} are represented by Eqs. 15 - 17, respectively:

$$OPEX = \sum_{p \in \boldsymbol{P}} \sum_{ut \in \boldsymbol{UT}} v_{ut} U_{ut,p} + \sum_{p \in \boldsymbol{P}} \sum_{ch \in \boldsymbol{CH}} v_{ch} F_{ch,p}^{CH} + C^{WT} + FOC \tag{15}$$

$$FSC = \sum_{c \in \boldsymbol{C}^{FS}} I_c q^{MAX} v_c \tag{16}$$

$$C^{WT} = q^{MAX} \varsigma^{WT} \tag{17}$$

where $U_{ut,p}$, and $F_{ch,p}^{CH}$ represent the usage of utility and flow of chemical in process $p \in \boldsymbol{P}$, respectively; v_{ut}, v_{ch}, and v_c (for $c \in \boldsymbol{C}^{FS}$) correspond to the unit prices of utility, chemical, and feedstock c; and ς^{WT} represents the unit wastewater treatment cost for per kg of feedstock.

The capital cost ($CAPEX$) is calculated in Eq. 18. The Lang factor β^{CAPEX} is estimated based on previous results reported by the National Renewable Energy Laboratory (NREL).[50] In essence, the capital cost is a factor multiplied by the total equipment cost:

$$CAPEX = \beta^{CAPEX} EC \tag{18}$$

The total equipment purchasing cost (EC) is the summation of equipment purchasing costs of all selected process:

$$EC = \sum_{p \in \boldsymbol{P}} EC_p \tag{19}$$

The equipment purchasing cost of process p is estimated using the power law of capacities for the specific unit, which accounts for the actual scale of the process:

$$EC_p = bc_p \left(\frac{\sum_{c \in \boldsymbol{C}} F_{c,p}^{IN}}{bs_p} \right)^{\alpha}, p \in \boldsymbol{P} \tag{20}$$

where bc_p is the base cost for base size bs_p of process $p \in \boldsymbol{P}$; α is the scaling factor, which is set to 0.6.

Due to equipment cost data being collected from various sources and reference years, the Chemical Engineering Plant Cost Index ($CEPCI$) is utilized to update the equipment costs estimated in the past to the year of analysis:

$$bc_p = bc_p^{REF} \left(\frac{CEPCI^{2021}}{CEPCI^{REF}} \right), p \in \boldsymbol{P} \tag{21}$$

where bc_p^{REF} is the equipment cost from the reference year, while $CEPCI^{2021}$ and $CEPCI^{REF}$ represent the Chemical Engineering Plant Cost Index values in 2021 and the cost reference year, respectively.

Moreover, the fixed operating cost (FOC) is calculated as a factor times the capital cost:

$$FOC = \beta^{FOC} CAPEX \tag{22}$$

where β^{FOC} is set to 0.03.[51]

4. Results and discussion

The resulting MINLP problem was solved in Pyomo v.6.2 using the BARON solver v.23.6.23.[52,53] The optimization model results were obtained using Windows 10, Intel Core i7-10700 CPU @2.9 GHz, 16 GB RAM. The base case was first evaluated, followed by a sensitivity analysis, and then the combined effects of significant parameters were studied. The main economic parameters in the base case are listed in Table 1, while other prices and costs can be found in Tables S4 and S5.

Table 1. Main economic parameters and assumptions

Parameter	Value
Plant life (year)	20
Working days (days/year)	330
Construction period (year)	3
Discount rate (%)	10
Tax (%)	21
Depreciation	Straight-line depreciation for 10 years
Capacity (dry metric ton/day)	2,000

4.1 Optimal biological lignin valorization biorefinery: base case scenario

In this section, we aim to identify optimal biological lignin valorization pathways, studying their costs, configuration, and energy consumption. We use NPV maximization as criterion for the selection of these pathways. The optimal lignin valorization pathways for different feedstocks are shown in Figure 3, which presents the material flows, along with the breakdown of costs and the structure of revenue. The overall optimum biorefinery pathway used softwood as feedstock (Figure 3(a)), but we also ran optimal pathways for hardwood and herbaceous feedstocks (Figures 3(b) and 3(c)). In our calculations, we use market prices for most of the products (PHA, biodiesel, and adipic acid). For PDC, a slightly different approach is used; since this product is not currently sold on a large scale, we use an estimated price of $5,500/MT, which is in line with the general price for biobased dicarboxylic acids.[54]

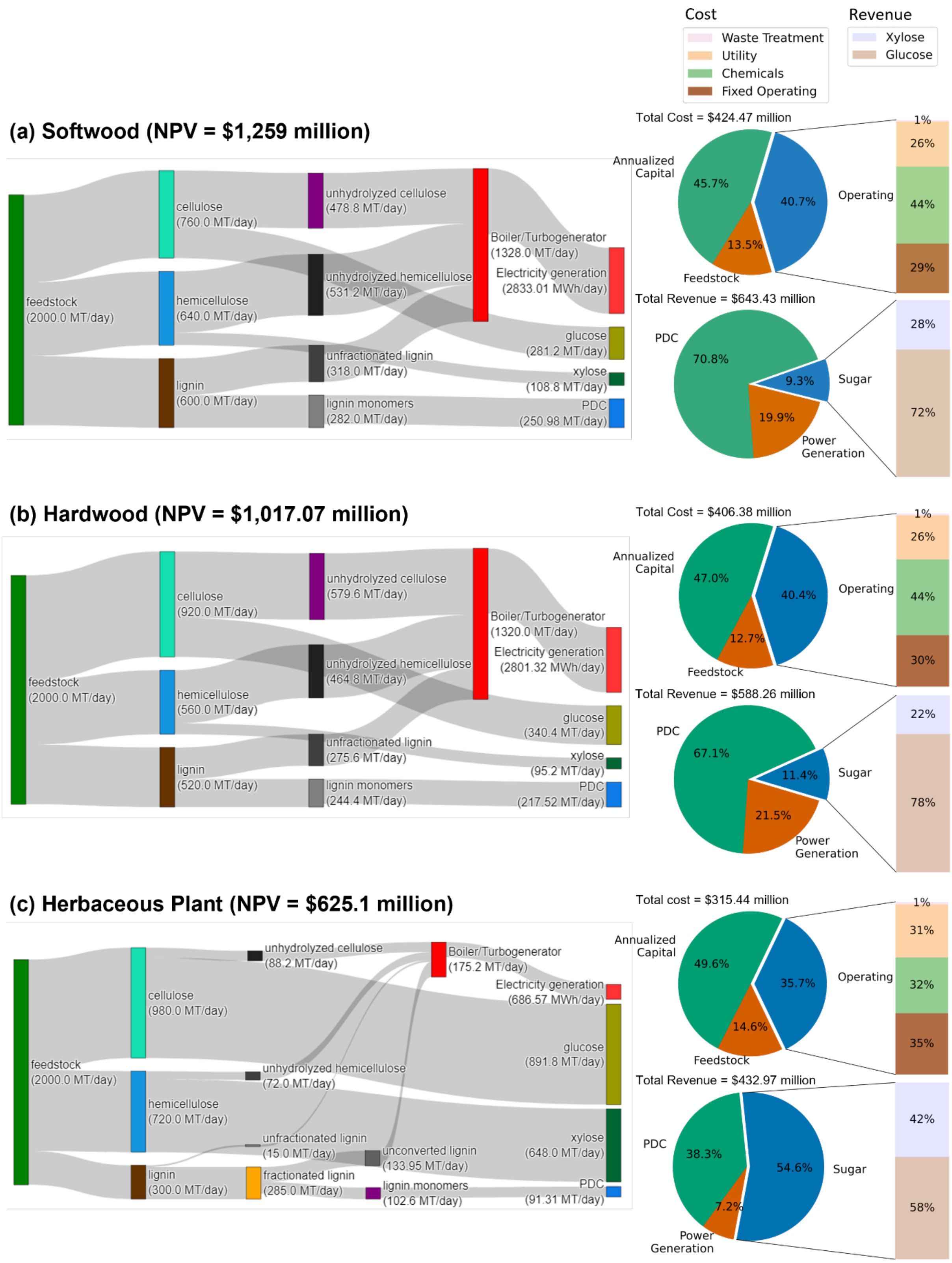
Cost
Waste Treatment
Utility
Chemicals
Fixed Operating
Revenue
Xylose
Glucose
(a) Softwood (NPV = $1,259 million)
feedstock (2000.0 MT/day)
cellulose (760.0 MT/day)
hemicellulose (640.0 MT/day)
lignin (600.0 MT/day)
unhydrolyzed cellulose (478.8 MT/day)
unhydrolyzed hemicellulose (531.2 MT/day)
unfractionated lignin (318.0 MT/day)
lignin monomers (282.0 MT/day)
Boiler/Turbogenerator (1328.0 MT/day)
Electricity generation (2833.01 MWh/day)
glucose (281.2 MT/day)
xylose (108.8 MT/day)
PDC (250.98 MT/day)
Total Cost = $424.47 million
Annualized Capital
45.7%
40.7%
13.5%
Operating
Feedstock
1%
26%
44%
29%
Total Revenue = $643.43 million
PDC
70.8%
9.3%
19.9%
Sugar
Power Generation
28%
72%
(b) Hardwood (NPV = $1,017.07 million)
feedstock (2000.0 MT/day)
cellulose (920.0 MT/day)
hemicellulose (560.0 MT/day)
lignin (520.0 MT/day)
unhydrolyzed cellulose (579.6 MT/day)
unhydrolyzed hemicellulose (464.8 MT/day)
unfractionated lignin (275.6 MT/day)
lignin monomers (244.4 MT/day)
Boiler/Turbogenerator (1320.0 MT/day)
Electricity generation (2801.32 MWh/day)
glucose (340.4 MT/day)
xylose (95.2 MT/day)
PDC (217.52 MT/day)
Total Cost = $406.38 million
Annualized Capital
47.0%
40.4%
12.7%
Operating
Feedstock
1%
26%
44%
30%
Total Revenue = $588.26 million
PDC
67.1%
11.4%
21.5%
Sugar
Power Generation
22%
78%
(c) Herbaceous Plant (NPV = $625.1 million)
feedstock (2000.0 MT/day)
cellulose (980.0 MT/day)
hemicellulose (720.0 MT/day)
lignin (300.0 MT/day)
unhydrolyzed cellulose (88.2 MT/day)
unhydrolyzed hemicellulose (72.0 MT/day)
unfractionated lignin (15.0 MT/day)
fractionated lignin (285.0 MT/day)
unconverted lignin (133.95 MT/day)
lignin monomers (102.6 MT/day)
Boiler/Turbogenerator (175.2 MT/day)
Electricity generation (686.57 MWh/day)
glucose (891.8 MT/day)
xylose (648.0 MT/day)
PDC (91.31 MT/day)
Total cost = $315.44 million
Annualized Capital
49.6%
35.7%
14.6%
Operating
Feedstock
1%
31%
32%
35%
Total Revenue = $432.97 million
PDC
38.3%
54.6%
7.2%
Sugar
Power Generation
42%
58%

Figure 3. Sankey diagram showing the material flow, and pie charts showing cost breakdown and revenue composition in the optimal scenario for three feedstocks (a) softwood (optimal case) (b) hardwood (c) herbaceous plant.

4.1.1 Optimal pathways cost and revenue configuration

In the case of softwood (shown in Figure 3(a)), the optimal process (milling, alkaline pretreatment, PDC fermentation) achieves the highest NPV at $1,259 million. This process results in daily production of 250.98 MT of PDC, along with coproducts glucose (281.2 MT) and xylose (108.8 MT), and an energy output of 2,833 MWh. The annual cost for this softwood-based biorefinery is $424.47 million, with annualized capital investments (CAPEX) at $194.13 million (45.7% of total) and operational costs (OPEX) at $172.93 million (40.7%). The revenue stands at $643.43 million annually, primarily from PDC (70.8%), energy generation (19.9%), and sugar coproducts (9.3%).

To further interpret the optimization results for different feedstocks, the optimization was run fixing the type of feedstock for hardwood and herbaceous plant. Hardwood, possessing the second highest NPV at 1,017.07 million USD, follows an optimal process pathway identical to that of softwood (Figure 3(b)), producing 217.52 MT/day of PDC, with glucose and xylose outputs at 340.4 MT/day and 95.2 MT/day, respectively. Its biorefinery costs are slightly lower at $406.38 million annually, with annualized CAPEX at $190.91 million (47% of total) and OPEX at $163.99 million (40.4%). Hardwood's revenue is $588.26 million, primarily from PDC (67.1%), energy (21.5%), and sugar coproducts (11.4%).

Herbaceous plants, with the lowest NPV of $625.1 million (Figure 3(c)), used a process involving milling, dilute acid pretreatment, base catalyzed depolymerization, and PDC fermentation, yielding 91.31 MT/day of PDC. They produce higher amounts of glucose (891.8

MT/day) and xylose (648 MT/day), with a daily energy output of 686.57 MWh. The biorefinery's annual cost is $315.44 million, led by CAPEX at $156.55 million and OPEX at $112.68 million. Feedstock costs are $46.2 million annually. The annual revenue is $432.97 million, mainly from sugars (54.6%) and PDC (38.3%), with electricity generation at 7.2%, showing a distinct revenue profile from softwood and hardwood.

In summary, PDC stands out as the most profitable product for all three feedstocks due to its high yield (Figure 2) and relatively high expected market price (Table S4 in **Supporting Information**). For woody feedstocks, alkaline pretreatment is employed, whereas herbaceous plants undergo dilute acid pretreatment and base catalyzed depolymerization. Given that hardwood and softwood contain a higher lignin content, which has a higher value post-upgrade, the optimal pathway for these feedstocks employs alkaline pretreatment, which depolymerizes lignin in-situ without requiring an additional depolymerization stage. Conversely, as herbaceous plants are more carbohydrate-rich, their processing aims to maximize revenue generation from this component.

The comparative cost and revenue configurations suggest that while softwood and hardwood generate higher revenues, they are accompanied by increased expenses. This positions them as potentially profitable yet economically intensive enterprises. Conversely, herbaceous plants present an alternative with lower revenue and expenses. Over an extended period, softwood and hardwood exhibit higher NPV.

4.1.2 Energy consumption for optimal biorefineries

Table 2 breaks down the yearly energy consumption for different feedstocks, tracking their usage of electricity, natural gas, and cooling water. The softwood biorefinery had the higher energy demand, consuming 217,404 MWh/year of electricity, 737,949 MWh/year of natural gas, and 424,718 MWh/year of cooling water. Hardwood biorefinery energy consumption is marginally lower, requiring 206,119 MWh/year, 665,001 MWh/year, and 376,889 MWh/year for electricity, natural gas, and cooling water, respectively. Herbaceous biorefinery, despite having a lower demand for electricity (163,685 MWh/year) and natural gas (585,571 MWh/year), exhibit a large requirement for cooling water at 557,915 MWh/year, notably during the biomass fractionation process which uses dilute acid pretreatment, in contrast to the alkaline pretreatment method used by the other two feedstocks. Furthermore, electricity generation from the boiler and turbogenerator —935 TWh, 924 TWh, and 227 TWh per year for softwood, hardwood, and herbaceous plants, respectively— exceeds the consumption needs of the biorefinery plant designs according to present assumptions, enabling the surplus to be sold externally, or consumed in other areas not accounted in our model (e.g., ethanol manufacturing). Environmentally, this excess production potentially provides a pathway to counteract the substantial energy demands and carbon and water footprints of each feedstock's processing cycle, especially if conventional energy sources are employed.

Table 2. Annual biorefinery energy consumption breakdown by feedstock type and processing stage

Feedstock type	Unit: MWh/year	Electricity	Natural gas	Cooling water
Softwood	Total	217,404	737,949	424,718
	Milling	132,000	0	0
	Fractionation	779	190,846	66,000
	Depolymerization	0	0	0
	Upgrading	84,624	547,103	358,718
	Energy generation	934,893,960	-	-
Hardwood	Total	206,120	665,002	376,889
	Milling	132,000	0	0

	Fractionation	779	190,846	66,000
	Depolymerization	0	0	0
	Upgrading	73,341	474,156	310,889
	Energy generation	924,436,498	-	-
Herbaceous plant	Total	163,685	585,572	557,915
	Milling	132,000	0	0
	Fractionation	785	359,324	417,998
	Depolymerization	110.99	27,196	9,405
	Upgrading	30,789	199,053	130,512
	Energy generation	226,567,757	-	-

4.1.3 Comparison analysis of processes with and without lignin valorization

Besides NPV, the internal rate of return (IRR) can be used to assess a project's profitability, representing the discount rate at which the NPV of all cash flows from a specific project is zero. A higher IRR suggests a more attractive investment, indicating a higher potential return. One key feature of the IRR is its independence from the interest rate.

For the optimal lignin valorization processes, the IRR was 25.63% for softwood, 22.71% for hardwood, and 19.45% for herbaceous plants, respectively. Despite herbaceous plants being available at a lower price, their biorefinery has the lowest NPV and IRR, primarily due to their lower lignin content. The critical importance of lignin valorization in biorefinery economics stems from the high value of processed lignin. Biomass with greater lignin content is thus more economically beneficial, as biorefineries that can convert lignin into final products can increase revenue enhancing their financial performance.

To understand the role of lignin valorization, we examine a scenario without lignin valorization.

In this case, the complete lignin fraction is sent the boiler and turbogenerator to generate energy, as opposed to being sent for depolymerization and further upgrading. In the absence of lignin valorization, the NPV for softwood, hardwood, and herbaceous plants biorefineries is -307.04, -219.27, and -35.56 million USD, respectively, while the IRR is 5.15%, 6.5%, and 9.4%, respectively (Figure 4). All three cases use dilute acid pretreatment as the method of fractionation. Herbaceous plants, when not subjected to lignin valorization, demonstrate relatively better results than woody feedstocks. These results suggest that under the prevailing technological conditions, lignin valorization with biological upgrading is economically preferable to directing all lignin to energy generation, and that process improvements that enhance lignin conversion yield or reduce costs could further enhance the economic viability of lignin valorization biorefineries.

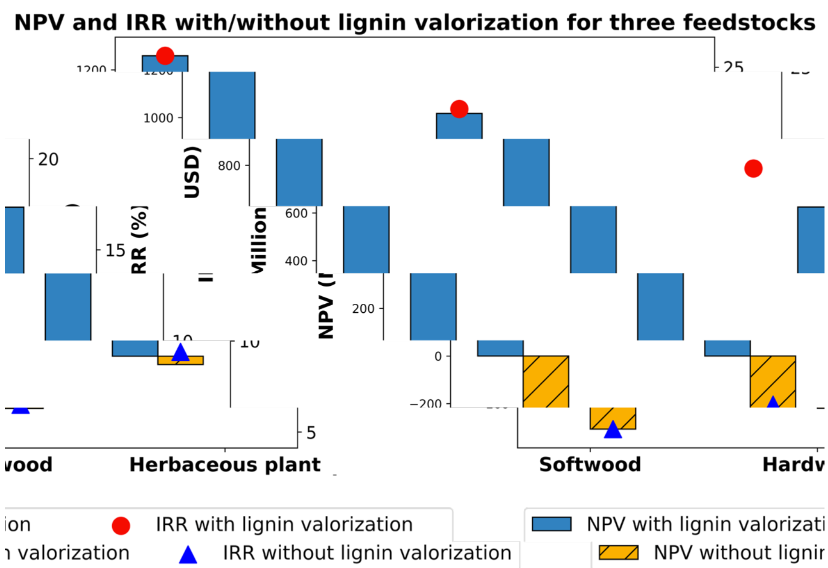

Figure 4. Comparative analysis of NPV and IRR for softwood, hardwood, and herbaceous biomass-based biorefineries, with and without lignin valorization

4.2 Sensitivity analysis

In our sensitivity analysis, we examine how variations in different parameters such as plant size, scaling coefficient, prices of feedstocks and products, distinct cost components, and process yield impact the NPV. The parameters in this sensitivity analysis are varied in a manner that covers their full potential range, from the lowest possible value to the highest, instead of moving along a fixed scale, which allows for a more comprehensive understanding of how extremes can affect the overall outcome. Details about the potential range of these variables are available in Table S7.

The sensitivity analysis reveals that PDC price is the most influential factor affecting NPV across all feedstocks (Figure 5). Specifically, a 50% increase in PDC price corresponded to increases in NPV for softwood, hardwood, and herbaceous plant cases by 1,505.13 (+120%), 1,304.45 (+128%), and 547.61 (+88%) million USD respectively. Out of all the scenarios, the woody feedstock displayed a higher sensitivity to changes in this parameter than herbaceous plants. The PDC yield is another pivotal factor; at its lowest value, the NPV for woody feedstocks could become negative, suggesting an unprofitable scenario.

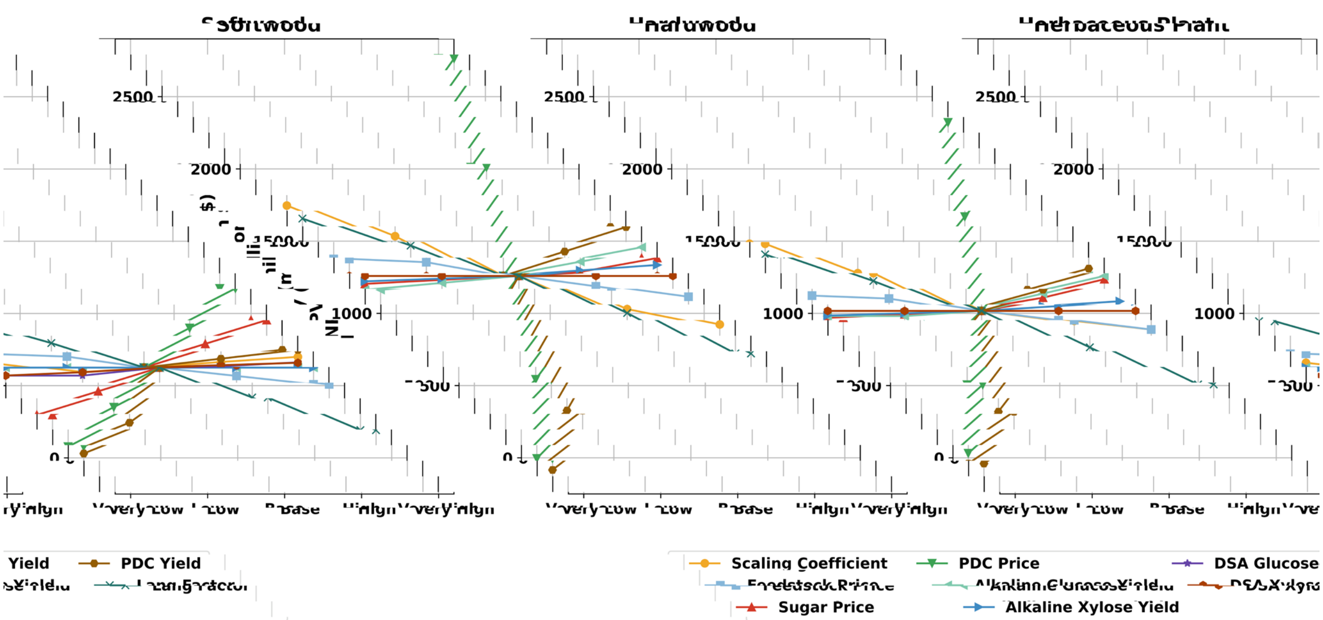

Figure 5. Spider diagrams of sensitivity analysis for lignin valorization biorefineries with biological upgrading for softwood, hardwood, and herbaceous plants

The Lang factor and the scaling coefficient are two additional significant parameters, especially since they relate to capital costs, which corresponds to a significant portion of the annualized cost. As the Lang factor moves from its base value, at 3.85, towards the lower end, at 3, NPV increases 397.05 (+32%), 390.48 (+38%), 302.2 (+51%) million USD for softwood, hardwood, and herbaceous plants, respectively. There is a notable increase in NPV for all types of feedstocks, with herbaceous plants showing a higher relative sensitivity.

For herbaceous plants specifically, a 50% reduction or increase in sugar prices corresponded to a decrease or increase in the optimal NPV by approximately 328.42 million USD (53%). In contrast, for softwood and hardwood, the optimal NPV decreased 4% and 5%, or increased 10% and 22%, respectively, under the same sugar price fluctuations. This is because the revenue from the herbaceous biomass biorefineries is dominated by the sugars sales (Figure 3).

Further sensitivity analyses, including the impact of plant size, are included in the **Supporting Information** (Figures S1 and S2 and Table S7).

4.3 Combined effects of significant parameters

In this section, we analyze the combined effects of fluctuations in final product prices and yields, as well as variations in the Lang factor and feedstock costs, on the NPV. This analysis will allow us to observe the influence of these critical factors when they interact, highlighting their combined impact on the NPV.

4.3.1 Effect of final product price and yield

The effects of final product pricing and biological upgrading yield on the optimal biorefinery NPV, with fixed selection of feedstock and final product, are shown in Figure 6. The prices of all chemical products are inherently variable but for the emerging products considered here the price is expected to vary considerably. Similarly, the yields from biological upgrading are subject to considerable variability due to technological advancements. We aimed to elucidate how potential changes in both yield and product price could create favorable conditions for lignin valorization and to identify scenarios where the valorization process becomes more economically viable, providing insights for future developments. Each heatmap in Figure 6 illustrates how the price and yield of the final products (PDC, PHA, biodiesel, and adipic acid) influence NPV, and the base case scenario is indicated on each plot. Red lines on the heatmaps represent the NPV break-even points; areas above are profitable, below are not. Black dashed lines show where the most cost-effective production pathway changes. The term "No lignin valorization" refers to conditions where upgrading lignin is not economically viable.

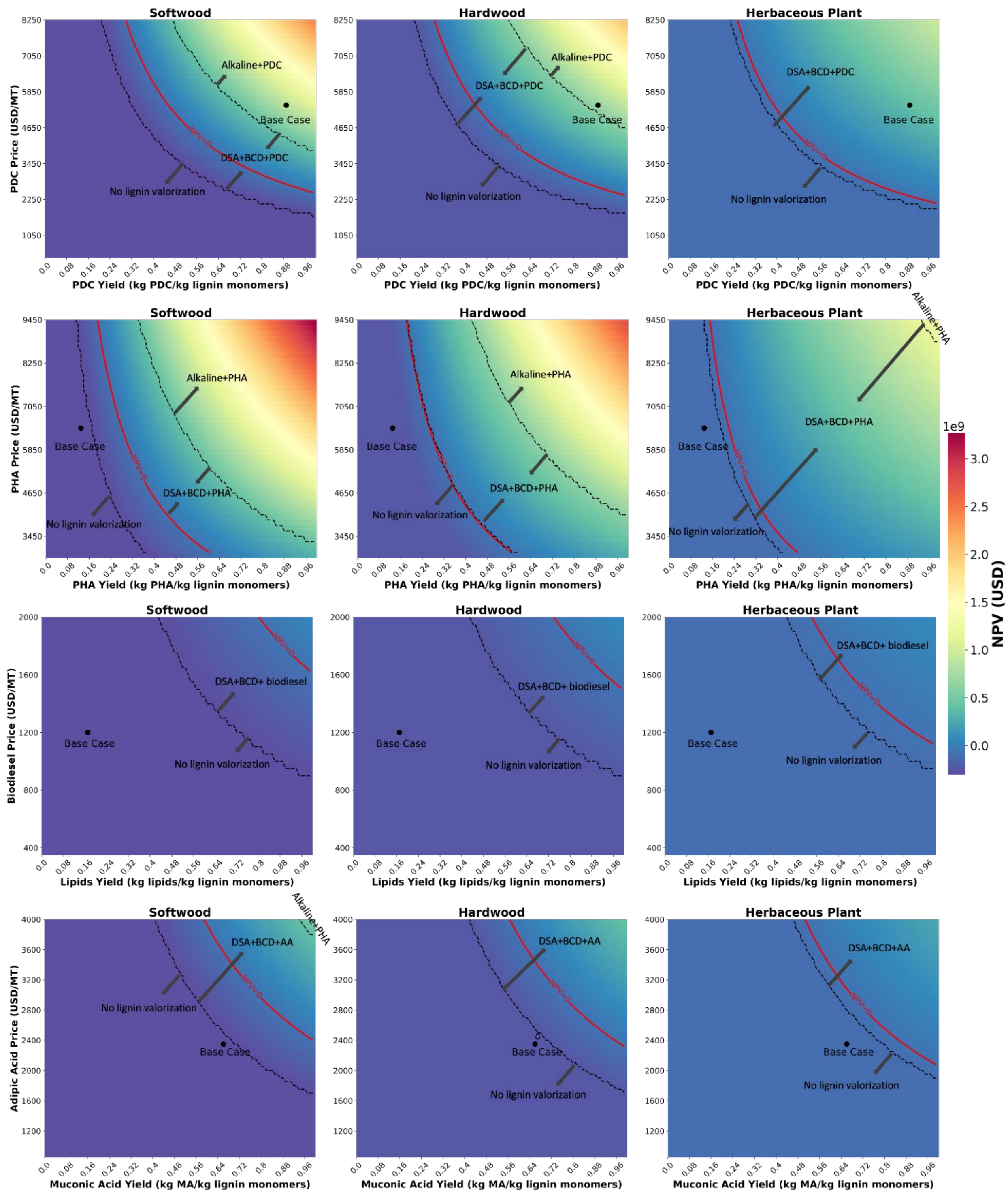

Figure 6. Heatmap of NPV with different final product (PDC, PHA, biodiesel, and adipic acid) price and biological upgrading yield for lignin valorization biorefineries for softwood, hardwood, and herbaceous plant. The black dashed lines show changes in the selection of the optimal

pathway. The red lines denote the threshold at which NPV equals zero, differentiating viable economic regions from non-viable ones.

The NPV of different products produced from various types of feedstocks is highly sensitive to the market price and the yield of the final products. When both price and yield are sufficiently elevated, alkaline pretreatment becomes the optimal method. As the price and yield drop, dilute acid pretreatment and base-catalyzed depolymerization become more favorable. However, in situations where the price and yield are low, it is preferable not to engage in lignin valorization at all. In such scenarios, the NPV can fall below zero, which signifies a lack of profitability and suggests that the investment would not be profitable (Figure 6).

The NPV for woody feedstocks exhibits a wider fluctuation in response to changes in product price and yield compared to that of herbaceous plants. Thus, woody feedstocks have a higher sensitivity to market dynamics and may offer greater economic opportunities or risks, depending on the prevailing market conditions and technological efficiency.

PDC stands out as the only final product exhibiting a positive NPV in the base case scenario, hinting at its potential profitability even under non-optimal conditions. This appears largely attributed to its high production yield. The analysis indicates that, should the price of PDC fall below $2,500/MT, PDC would cease to be profitable regardless of yield—this price represents the minimum threshold allowed by current technological advancements. To position PDC from lignin as a viable alternative to existing plastic precursors and enhance its market competitiveness, it would be important to keep the capital expenditure of the biorefinery low.

The provided context suggests that the production of PHA, when considering the base case scenario, is not economically viable due to low yields and the current price point. However, if there could be an improvement in the yield through biological upgrading—specifically, if the yield could be increased to 30%—along with maintaining robust market prices, PHA production could potentially become profitable, as indicated by achieving a positive NPV.

In contrast, the outcome for biodiesel and adipic acid is less favorable. The process of lignin valorization through biological upgrading does not seem to provide an economically viable path for these products under present market conditions. This is attributed to the inability of these commodities to achieve a premium price in the market, which is necessary to offset the production costs and achieve profitability. Essentially, without the ability to sell these products at a higher price, there is a lack of profitable scenarios for these products, even if lignin valorization could be effectively implemented at high yields.

4.3.2 Effect of feedstock price and capital cost

The biorefinery initial capital investment is calculated based on the Lang Factor, a multiplier used to estimate the total capital cost from the purchased equipment cost. Changes in the Lang Factor used in the analysis can lead to big differences in estimated costs, and, consequently, affect the expected financial feasibility of the project. In parallel, it is crucial to address the variable nature of feedstock prices, which can be subject to fluctuations based on availability, demand, and logistical costs.

Lower feedstock prices coupled with a smaller Lang factor, lead to a higher NPV across all feedstock types. The heatmaps for each feedstock highlight a threshold effect (red line)—if the feedstock cost and Lang factor increase beyond a certain point, the NPV falls into negative region (Figure 7).

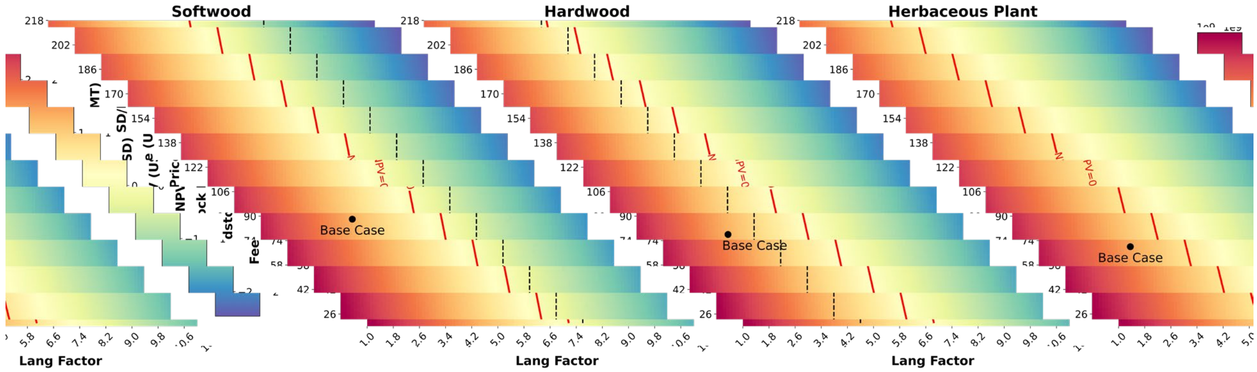

Figure 7. Heatmap of NPV with different feedstock price and Lang factor. The black dashed lines represent the boundaries for the optimal processing pathway selection. The red lines represent the breakeven point where NPV is zero.

The feedstock price does not affect process selection. For softwood, when the Lang factor is below 7.6, alkaline pretreatment is the preferred method. In contrast, for hardwood, this preference shifts to alkaline pretreatment when the Lang factor is below 4.6. When the Lang factor rises above these points for softwood and hardwood, respectively, the preferred processes switch to dilute acid pretreatment and base-catalyzed depolymerization. For herbaceous plants, dilute acid pretreatment and base-catalyzed depolymerization are favored regardless of the Lang factor or feedstock price. These insights allow for a nuanced understanding of how operational costs influence process selection in the pursuit of economic viability in lignin valorization biorefineries.

5. Concluding remarks

In this study, we developed a deterministic optimization model for a lignin valorization biorefinery system with biological upgrading using Pyomo, a Python-based, open-source optimization modeling framework. We made our code publicly accessible, which we anticipate will serve as a valuable resource for further analysis of lignin valorization biorefineries for researchers and engineers.

The findings from our model underscore the significance of the price and yield of lignin-derived products on the biorefinery profitability. Our evaluation suggests that products such PDC from lignin offers lucrative prospects, while PHA emerge as products with considerable potential. On the other hand, the production of biodiesel or adipic acid from lignin seems to offer weaker economic benefits. The preferred process depends on the scale of lignin valorization and the economic performance of the final products. When operating a high throughput biorefinery system or when final product prices and yields are high, or if the initial investment is modest, an alkaline pretreatment approach is advantageous. Conversely, dilute acid pretreatment followed by base-catalyzed depolymerization is favored when these factors are less optimal. Further work on quantifying the environmental considerations of the different process could shed light on their differential benefits and impacts, and provide optimization tools beyond profitability indicators.

ASSOCIATED CONTENT

Supporting Information

Code Availability:

The source code utilized in this study is available for access and review. It can be found in our dedicated GitHub repository. Please visit the following link to view and download the code: https://github.com/Kankincredible/lignin-valorization-superstructure-optimization.

Data Accessibility:

All data supporting the findings of this research are included within a PDF file. This file contains detailed datasets and supplementary information essential for understanding the study's results.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MINLP: mixed integer nonlinear programming

MILP: mixed integer linear programming

NREL: National Renewable Energy Laboratory

DSA: dilute acid pretreatment

SEP: steam explosion

LHW: liquid hot water

Organosolv: organosolv pretreatment

AFEX: ammonia fiber explosion

GVL: gamma-valerolactone pretreatment

Alkaline: alkaline pretreatment

BCD: base catalyzed depolymerization

HDO: hydrodeoxygenation

HTU: hydrothermal upgrading

HDG: catalytic hydrogenolysis

PHA: polyhydroxyalkanoates

MA: muconic acid

AA: adipic acid

PDC: 2-Pyrone-4,6-Dicarboxylic Acid

NPV: net present value

CF: cash flow

AR: annual revenue

FSC: feedstock purchasing cost

$OPEX$: *operating cost*

$CAPEX$: *capital investment*

FOC: *fixed operating cost*

EC: *equipment cost*

DP: *depreciation*

CEPCI: Chemical Engineering Plant Cost Index

Indexes

FS: *feedstock*

PM: *polymers*

MILL: milling

FR: *fractionation*

DPL: *depolymerization*

UPG: *upgrading*

BURN: boiler and turbogenerator

CP: *coproducts*

FEED: feeding

PROD: product

IN: inflow

OUT: outflow

$\boldsymbol{C}$: *component set*

c, c': *index of components.* $c, c' \in \boldsymbol{C}$

$\boldsymbol{P}$: *process set*

p, p': index of processes. $p, p' \in \boldsymbol{P}$

$\boldsymbol{K}$: the set mutually exclusive superstructure stages, which has the following elements: biomass fractionation, lignin depolymerization, or biological upgrading

$\boldsymbol{UT}$: utility set

ut: utility. $ut \in \boldsymbol{UT}$

$\boldsymbol{CH}$: additional chemicals set

ch: additional chemicals. $ch \in \boldsymbol{CH}$

$\boldsymbol{T}$: year set

t: year. $t \in \boldsymbol{T}$

REF: reference year

Parameters

$\xi_{c,c'}$: composition of polymer (cellulose, hemicellulose, and lignin) c in feedstock (softwood, hardwood, and herbaceous plant) c'

$x_{p,p'}$: the relationship between process p and q. $x_{p,p'} = 1$: there is flow from process p to process q; $x_{p,p'} = 1$: otherwise

$\mu_{ch,p}^{CH}$: additional chemicals ch consumption ratio in the process p

$\mu_{ut,p}^{UT}$: utility ut consumption ratio in the process p

$\theta_{c,c',p}^{OUT}$: yield of product c' from component c in process p

M: big-M coefficient

v_c: price of product c

v_{ut}: price of the utility

v_{ch}: price of the additional chemicals

ν^E: *price of the energy from boiler and turbogenerator*

q^{MAX}: *maximum flow from feedstock*

bc_p^{REF}: *base equipment cost of process p from the reference year*

bs_p: *base size of process* p

bc_p: *base capital cost of process p on the base of* bs_p

β^{CAPEX}: *Lang factor*

β^{FOC}: *fixed operating cost factor*

r: *interest rate*

tax: tax rate

f_t : *fraction of capital expenditure spent at year* t

α: *scaling coefficient*

η: *boiler and turbogenerator efficiency*

ρ_c: *lower heating value of product c*

ς^{WT}: *unit wastewater treatment cost for per kg of feedstock*

Variables

I_p: *binary variable. Selection of process* p

I_c^{FS}: *binary variable. Selection of feedstock* c

$F_{c,p',p}$: *flow of component c from process* p' *to process p*

$F_{c,p}^{IN}$: *inflow of component* c *in process* p

$F_{c,p}^{OUT}$: *outflow of component* c *to the next stage in process* p

$F_{c,p}^{CP}$: *outflow of coproduct* c *in process* p

$U_{ut,p}$: *utility* ut *used in process* p

$F_{ch,p}^{CH}$: *additional chemicals* ch *used in process* p

$E_{c,p}^{OUT}$: *electricity generated by boiler and turbogenerator*

C^{WT}: *waste treatment cost*

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