



Cite this: *Green Chem.*, 2024, **26**, 4092

Design of an integrated biorefinery for bioethylene production from industrial forest byproducts†

Rocio Elizabet Cardozo, *‡, Nicolás Martín Clauser, ‡
Fernando Esteban Felissia, ‡, María Cristina Area and María Evangelina Vallejos

The global forest industry is focused on developing waste valorization technologies. Regional resources use in biorefineries could be a strategy to improve profitability and mitigate the environmental impact of the involved industrial sectors, adding a new value chain to the forest industry. This study develops the mass and energy balance for bioethylene and lignin production from industrial pine sawdust (IS), a primary wood processing in Argentina. The proposed production process is composed of: (i) soda-ethanol pretreatment to remove the lignin; (ii) simultaneous saccharification and fermentation (SSF) to convert the cellulose to glucose and then to ethanol; (iii) ethanol recovery (95%); (iv) ethanol dehydration to bioethylene and; (v) bioethylene recovery through an ethylene tower and stripper. In the proposed process, 107 kg of bioethylene per ton of dry sawdust could be obtained, recovering 208 kg of lignin. Energy consumption is about 1885 MW h t⁻¹ of dry sawdust. The highest consumption is in pretreatment and ethanol recovery processes, which can be reduced by 42%. Regarding economic assessment, the internal rate of return (IRR) and net present value (NPV) were 10.08% and 5.21 MM USD, respectively. Sensitivity analysis shows that the most influential parameters are lignin and bioethylene market prices and energy and enzyme costs.

Received 19th January 2024,
Accepted 26th February 2024

DOI: 10.1039/d4gc00327f

rs.c.li/greenchem

Introduction

The use of renewable resources has become ever more frequent, and its growth worldwide continues with the proposal to reduce the environmental effects of the oil-based economy by employing the biorefinery process advantages.¹ The indiscriminate use of fossil resources and the increase in environmental pollution sparked a discussion about the long-term implications for future generations; therefore, many countries have begun to identify policies to mitigate the effects.^{2–4} The industrial forest waste available in Argentina, more precisely in the Northeast Region (NEA), does not compete with food raw materials (crops rich in starch or vegetable oil) because they are non-edible waste; they are not used according to their potential, but wasted by burning or laying on floors.^{5,6} Its chemical composition consists of cellulose, hemicelluloses, and lignin, making it strategically usable for a wide range of products within a biorefinery framework.⁷ Pine is one of the most relevant forest raw materials in the NEA region of

Argentina. In the sawmill valorisation chain, several byproducts are generated in large amounts. One of these byproducts is sawdust, which represents about 9% of the total processed feedstock.⁸ Pine sawdust could be a promising raw material to produce second-generation ethanol (2G ethanol) and its many derivatives as bioethylene-based products. Bioethylene production requires sawdust fractionation into its main components, the application of effective purification processes, and its cost-effective conversion into monomers and platform molecules. The process design and a technical and economic evaluation are required to develop and consolidate the biorefinery schemes on an industrial scale.

Some studies have been reported on the production of bioethylene and byproducts in the last few years. For example, a study analysed the processing of beech wood employing an ethanol–water mixture catalysed with 1% sulfuric acid followed by enzymatic hydrolysis. The main obtained bioproducts were 0.1 t bioethylene, 0.16 t organosolv lignin per dry tonne of beech wood, and others.⁹ In this study, bioethylene production from industrial sawdust generated 0.107 t of product and 0.208 t of lignin.

The concentration of bioethanol is also relevant. In other words, using 42 194 t h⁻¹ of pure bioethanol (95%) feed stream, 21 876 t h⁻¹ of bioethylene was produced.^{10,11} However, 45.0614 t h⁻¹ bioethylene was obtained from 165 t h⁻¹ of a diluted, less concentrated renewable ethanol feed.¹⁰

IMAM, UNaM, CONICET, FCEQYN, Programa de Celulosa y Papel (PROCyP), Misiones, Argentina, Félix de Azara 1552, Posadas, Argentina.

E-mail: rociocardozo10@gmail.com; Tel: +5493743-439529

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4gc00327f>

‡ These two authors contributed equally to this work.

Several authors also report that the selling price of biorefinery products greatly influences the model sensitivity.^{9,10,12,13} The cost of electricity has also been a relevant factor.^{14,15} Regarding the raw material, industrial sawdust availability¹⁶ and cost^{9,12} are critical factors in some studies. In contrast, in the NEA region of Argentina, the feedstock cost is relatively low.

A few years ago, the competition between the price of ethylene of petrochemical origin and bioethylene was impossible because of the wide gap in costs; however, the difference has now been reduced and this has made it possible for biorefineries to produce bioethylene with a competitive capacity to operate in the world.¹⁷ It has been shown that bioethylene for ethylene-based polymers significantly reduces greenhouse gases without changing the properties of the biobased polymer.¹⁸

The optimization of the process lines of biorefineries encompassing technical, environmental, and economic aspects has been the subject of intense research in recent years.^{19–22} These studies highlighted that more studies are needed to (i) reduce costs of enzymatic hydrolysis by improving the conversion process of lignocellulosic material to fermentable sugars,²³ (ii) optimize bioethanol production technology,²⁰ (iii) use of less purified bioethanol for cost and energy savings,²⁰ (iv) reduce the influence of impurities in bioethanol on the efficiency of the catalytic process of ethylene production,²⁰ (v) develop of catalysts for bioethanol conversion to ethylene at low temperature.²¹

Ethylene production costs and yield widely vary depending on the lignocellulosic raw material selected and on the location of the plant.¹¹ A lignocellulosic waste-integrated biorefinery could be a strategy to produce bioethylene, where the 2G bioethanol is the main product obtained from cellulose.

This work aims to design an integrated biorefinery for bioethylene production from pine sawdust waste, identifying the higher energetic consumption stages and the potential chemical recovery to implement a biorefinery at the industrial scale. In addition, a risk and sensibility analysis of the production process was carried out considering the uncertain or unavailable data.

Experimental

Bioethylene production process

Bioethylene production was selected as the main product in the present study, and its valorization in a biorefinery platform was assessed. The process proposed for bioethylene production from pine sawdust is shown in Fig. 1.

Raw material

Pine sawdust was selected as raw material. Its chemical composition, determined in previous works, is 40.9% glucans, 7.45% xylans, 2.58% galactans, 0.77% arabinans, 14.8% mannans, 2.28% total extractives, 29.2% lignin.²⁴

Soda-ethanol pretreatment

The sawdust is partially delignified using a soda-ethanol pretreatment. It is carried out at liquid-to-solid ratio (LSR) of

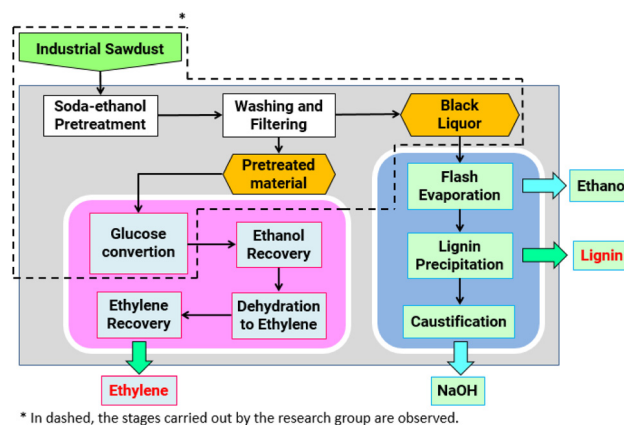


Fig. 1 Simplified scheme of the proposed process.

5.44 : 1, 170 °C, EtOH/H₂O ratio (% v/v) 35/65, and 23.3 NaOH (% w/w) during 140 min. The pretreatment was carried out in a pressurized M/K reactor, and after pretreatment, the pulp was washed with five-cycle water.²⁵ The present study assumed that pine sawdust pulp is washed at a 3.5 kg water per kg dry pulp ratio (reported industrial values).²⁶ The washed material was centrifuged after each washing step. The chemical composition of the pretreated material is 80.18% glucans, 7.20% xylans, 0.29% galactans, 8.40% mannans, and 3.67% lignin.²⁴

Ethylene production

The pretreated material is sent to the simultaneous saccharification and fermentation (SSF) step, where Cellic® CTec2 commercial enzymes are used for the enzymatic hydrolysis, and *Saccharomyces cerevisiae* is applied in fermentation.²⁴ An ethanol yield of about 99% was determined in previous studies reported by our research group.²⁴ Similar values were found in the literature.^{27,28} Other studies at the pilot scale reported yields of about 95–96% of theoretical values, using enzyme charges between 15–25 kg of enzyme protein per ton of cellulose.²⁹ The present study assumes an enzyme charge of 10 FPU and an ethanol yield of 96% of the theoretical value. Besides, in the ethanol fermentation process, highly pure CO₂ is generated in a ratio of 51% of ethanol and 49% of CO₂.³⁰ After enzymatic hydrolysis and fermentation, ethanol is recovered (at a concentration of 95%³¹). Ethanol conversion to ethylene uses catalysts like modified Zeolite HZSM-5, γ-Al₂O₃, and Al₂O₃.^{32–35} Usual process temperatures are between 240 °C and 500 °C. In recent years, H-ZSM-5 has been converted into a promising commercially valuable alternative for ethanol dehydration to ethylene due to its high conversion rate, selectivity, and stability.³⁶ The catalyst can be completely regenerated.^{37,38} Also, previous studies reported that catalysts and reagents in ethanol to ethylene conversion costs represent less than 1% of total operating costs; therefore, catalyst costs were considered negligible.^{10,39,40} In the present study, ethanol is converted to ethylene in the catalysis step using an HZSM-5 zeolite catalyst with an ethylene conversion of 99% and stabi-

lity of 630 h.⁴¹ Finally, ethylene is purified using a conventional operation involving cooling and separation columns.^{10,11}

Operational conditions

The selected conditions are presented in Table 1.

Lignin and NaOH recovery

The liquid stream after solvent recovery is composed mainly of lignin and NaOH. NaOH must be recovered to be reused in the process. Lignin could be recovered as a byproduct of acidification^{42,46} using CO₂,^{42,47} one of the most used reagents. The advantage of CO₂ is that it is a component of the gases generated in the boiler in the caustic recovery process. At pH values about 7–9, recovery yields of lignin could be up to 85%,⁴² and using CO₂, the pH of the black liquor could decrease lower than 9. After CO₂ acidification, H₂SO₄ is added to reach a pH of 3. The present study assumed that all CO₂ from the boiler is used to recover lignin. After lignin recovery, NaOH must be recovered to reach the process economy.

The usual process to recover NaOH is causticization. The liquid stream coming from lignin recovery still contains sugars (311 kg), lignin (69 kg), and NaOH (35 kg). The stream from lignin precipitation must be concentrated in a multiple-effect evaporator to reach a solid concentration of 60–80%.^{44,45} Afterward, the stream is burned in a recovery boiler, generating energy with NaOH recovery.⁴⁵ The solid material in the furnace is composed of sodium carbonate (Na₂CO₃), which reacts with calcium hydroxide Ca(OH)₂, generating calcium carbonate

(CaCO₃) and NaOH. Ca(OH)₂ is regenerated from CaCO₃ through CaO conversion and then hydrated with H₂O. Carbon dioxide (CO₂) is also generated in this last reaction.^{45,48} Caustic recovery has up to 90% efficiency in a typical Kraft recovery process,^{45,48} so, in this study, it was assumed that 85% of NaOH is recovered.

Mass and energy balances

The total energy consumption is calculated as the sum of the different energy inputs for bioethylene production. In organosolv process, energy consumption was calculated based on the heating values of each component (kJ kg⁻¹ °C), the amount of each component (kg), and assuming that the temperature variations are between room temperature (25 °C) and working temperature (170 °C). The assumed energy for the SSF stage is 1.7 kW h kg⁻¹ of ethanol.⁴⁹ The energy required for the ethanol recovery is 1.9 kW h kg⁻¹ ethanol based on distillation to 95% concentration.^{50,51} A final temperature of 240 °C was considered for ethanol dehydration.⁴¹ For the ethylene recovery stage, it is assumed that 0.3 kW h kg⁻¹ of recovered ethylene.³⁹

It is assumed that a recovery of 99% by flash evaporation and one distillation column for the solvent (ethanol) used in the pretreatment and then recycled.^{52,53} The energy consumed in this recovery step is considered negligible due to the high temperature of the liquor at the outlet and ethanol concentration.

The energy generated in the recovery boiler (caustic recovery) was assumed to be 2.5 kW h kg⁻¹ of liquor, based on the lower heating value of the liquor with 80% of solids.⁴⁴ All energy generated in the recovery boiler is assumed to be used for the causticization.⁴⁵

For chemical processes, energy sources commonly depend on the sources available in the region. The most common energy sources used in the NEA region are steam and electricity due to their availability. In this sense, 8–13% of total energy comes from electricity, and the remaining energy comes from steam.^{54,55} Besides, the usual steps that use electricity are saccharification, fermentation, distillation, and ethylene conversion.^{55–57} In the present study, it was assumed that for the total energy used for SSF and distillation, 0.74 kW h kg⁻¹ of ethanol is for electricity.^{55,56} Besides, for ethylene conversion, it was assumed that for the total energy consumed in ethanol to ethylene conversion, 0.052 kW h kg⁻¹ of ethanol corresponds to electricity.^{56,57}

Finally, energy integration (or heat integration) is one strategy to reduce energy consumption. The heat integration aims to reduce energy costs by reusing the heat energy in the process streams. For this purpose, the streams with values of $m \times C_p > 750 \text{ kJ s}^{-1} \text{ °C}$ were considered, where m is flow (kg s⁻¹), and C_p is the heat capacity of the stream (kJ kg⁻¹ °C). Also, a loss coefficient of 10% of the calculated energy was assumed.⁵⁸

Economic assessment

In the first step, the total capital investment (TCI) is calculated from the total equipment cost based on integrated processes, including all equipment and associated capital costs. In the

Table 1 Operational conditions for ethylene production

Step	Description	Ref.
Soda-ethanol pretreatment ^a	LSR 5.44 : 1 170 °C EtOH : H ₂ O 35% to 65% v/v NaOH 23.3% w/w, 140 min	24
Washing ^a SSF ^a	3.5 kg water per kg dry pulp Celli CTec 2 <i>Saccharomyces cerevisiae</i> 37 °C 10 FPU g ⁻¹ cellulose 96% conversion	26 24 and 27
Ethanol recovery	95% concentration for distillation 2 column distillation	31
Ethanol dehydration	Catalyst nanoscale HZSM-5 zeolite Selectivity 98% Stability 630 h Ethanol conversion 99%	41
Ethylene recovery	Cryogenic distillation column	11
Lignin recovery	75% recovered from black liquor pH 8 with CO ₂ pH 3 with H ₂ SO ₄ 0.3 kg kg ⁻¹ of lignin and 10% re- entry	42 and 43
NaOH recovery	Multiple-effect evaporator: solid concentration of 60–80% Causticization process efficiency: 85%	44 and 45 42

LSR: liquid solid ratio. ^a Stages of the process were developed in the laboratory by members of the group.

second step, variable and fixed operating costs are determined. Variable operating costs involve raw materials, waste handling, and byproduct credits, and fixed operating costs include labor and various other items. Finally, a discounted cash flow analysis allows for determining the net present value (NPV) and internal rate of return (IRR). The economic parameters of bioethylene production in an integrated biorefinery from industrial forest byproducts were used to assess the potential of this product and its byproducts.⁶⁴

For the design process, an economic feasibility assessment was developed. Operational costs, fixed and variables, and total investment costs were determined.^{65–67}

The equipment costs were calculated using the factors proposed by references.^{66,68} Besides, the equipment costs were determined using eqn (1).

$$C = C_o \left(\frac{M}{M_o} \right)^n \quad (1)$$

C is the equipment cost of a plant with a capacity of M , C_o is the reference cost of a plant with a capacity of M_o , and n is an exponent smaller than one (between 0.6–0.8).

Different scaling factors, installation costs, and other costs were determined from the bibliography.^{65–67,69}

Finally, as economic indicators, the IRR and the NPV were selected because they are usually employed for investments in biorefinery projects.^{65,70} The following variables were selected for the economic analysis (Table 2).

Sensitivity assessment

The TCI and cash flows are affected by changes in raw materials, other operating costs, and sales volume and price. These uncertainties can be estimated through sensitivity analysis after the investment and cash flows are calculated. In the sensitivity analysis, various economic parameters are adjusted, supposing a range of errors for each one. Then, it determines how sensitive the economic parameters are to the error vari-

ation, which is plotted as NPV vs. the parameter studied. Finally, the degree of risk involved in the performance of integrated biorefinery is projected.⁶⁴

This analysis assesses the influence of the selected variables on the overall process. One of the usual methods is the one-at-a-time test, which consists of varying one variable and keeping the other variable fixed. The present study used the sensitivity assessment to evaluate how several variables affect the NPV forecast. Crystal Ball software was used for model simulation. After selecting the variables, their limits and adjusted curves have to be defined.^{16,71}

The variables that most affect the profitability of the proposal are economic factors,^{13,16} for example, selling prices,^{10,13} feedstock^{72,73} and reagents⁷⁴ costs, others; and technical or operational factors,⁷⁵ for example, the LSR of pretreatment, the steam economy, and others.⁷¹

Table S1 of the ESI† shows each factor considered in the present study. Their probability distribution and the limits of uniform and triangular distributions were selected from the updated bibliography. The variables assigned to the normal distribution used deviations of 10%.

Results

Technical assessment

The general scheme evaluated for bioethylene production is shown in Fig. 2. In this figure, the mass and energy balance of the proposed process is presented. The main products are bioethylene and lignin.

The analysis determined that 107 kg of bioethylene and 208 kg of lignin could be obtained from 1000 kg of industrial pine sawdust (IS). After SSF, 9 kg of cellular mass from yeast is recovered, which can be harnessed for energy generation purposes.⁷⁶ Besides, 178 kg of CO₂ (highly purity gas) is produced in fermentation.⁷⁷ The CO₂^F (CO₂ coming from fermentation) could be sold as a byproduct after CO₂ purification.⁷⁸ In the present study, CO₂ byproduct was not included in the assessment. Regarding the used reagents, it is possible to recover 198 kg of NaOH and 1458 kg of ethanol used in the soda-ethanol pretreatment. Concerning the energy consumption shown in Fig. 2, soda-ethanol pretreatment requires 1005 kW h, whereas 347 kW h are needed for the SSF stage, 436 kW h for ethanol recovery, 22 kW h for ethanol dehydration, 33 kW h for lignin recovery and purification, and 42 kW h for ethylene recovery. Overall consumption per ton dry of IS. The energy consumption for the overall process is 1792 kW h per ton of industrial sawdust. The pretreatment represents the highest energy consumption, followed by the ethanol recovery stage, representing more than 70% of energy consumption (see Fig. 3). Previous studies have shown similar results concerning the processing of electricity.^{9,79}

Due to the high energy consumption, heat recovery from the three hot streams and two cold streams was analysed. Available heat was 484 kW h per ton IS for hot streams and

Table 2 Unit values used in variable operating costs for the techno-economic assessment

Variables unit prices at the mill gate	Value	Ref.
Sawdust (t y ⁻¹)	200 000	59
Sawdust (USD t ⁻¹)	9	60
Energy (USD kW h ⁻¹)	0.08	^a
Steam (USD t ⁻¹)	10	^a
Water (USD m ⁻³)	0.6	^a
Labor (USD h ⁻¹)	6–31	Assumption
Tax rate	35%	Assumption
<i>Chemicals</i>		
Ethanol (USD L ⁻¹)	0.7	61
NaOH (USD kg ⁻¹)	0.6	Assumption
H ₂ SO ₄ (USD kg ⁻¹)	0.09	43
Enzymes (USD kg ⁻¹)	10	Assumption
Waste treatment (USD m ⁻³)	0.8	Assumption
<i>Products</i>		
Bioethylene USD t ⁻¹	1500	9 and 31
Lignin USD t ⁻¹	900	62 and 63

^a Costs correspond to argentinian values.

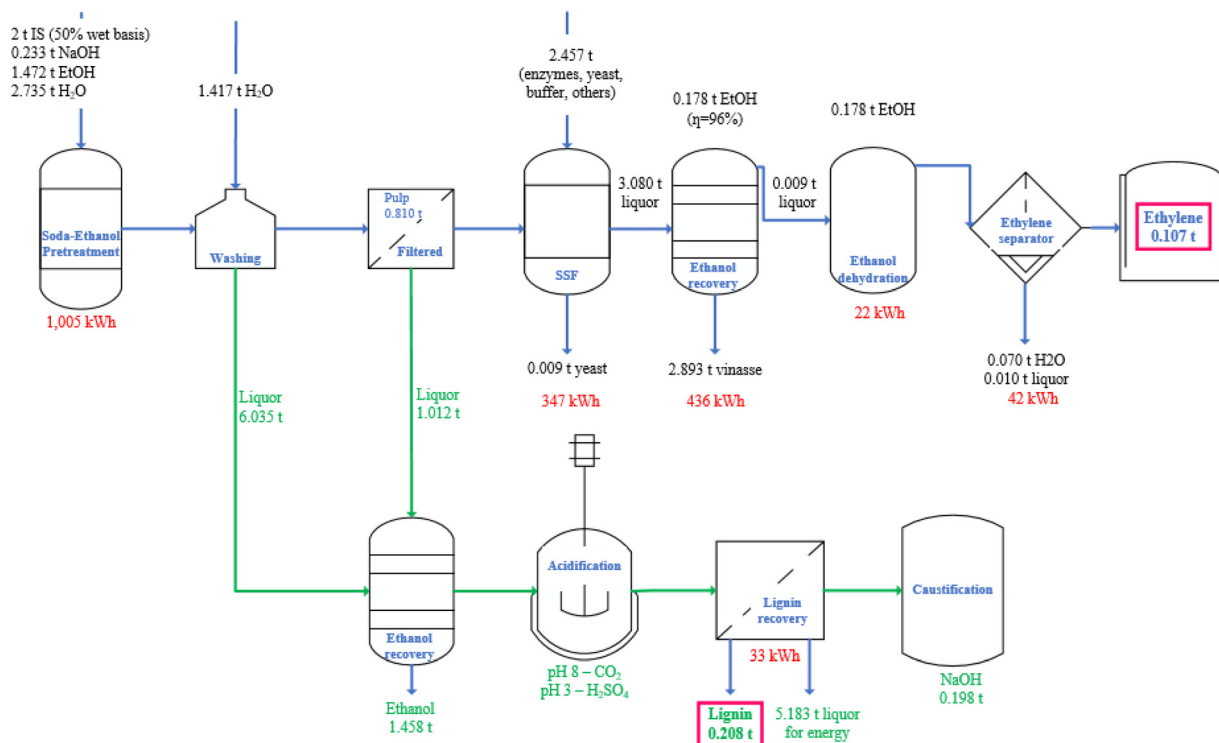


Fig. 2 Process diagram of the bioethylene production through the soda ethanol process.

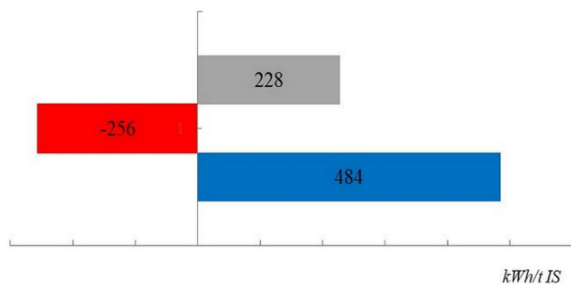


Fig. 3 Energy available from integration.

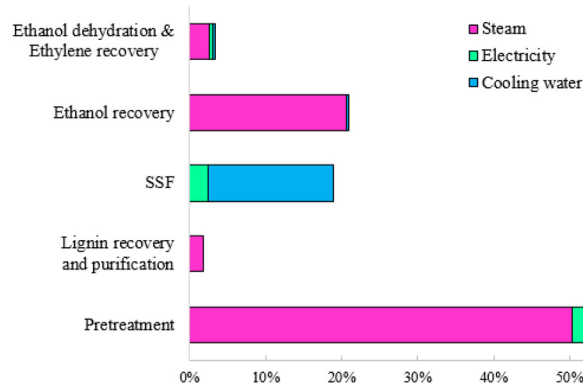


Fig. 4 Comparison of energy consumption in each stage of the process.

256 kW h per ton IS for cold streams. Thus, the overall consumption of the process can be reduced by 42% (see Fig. 4).

Economic assessment

After the mass and energy balance, the economic assessment was carried out. Table 3 presents the capital investment. The total investment costs were determined based on the factors used by the NREL.⁶⁸

Initially, fixed and variable costs were determined (see Fig. 5). The main impacts in variable costs are due to steam and electricity and the cost of enzymes, whereas general maintenance is the chief fixed cost. Table 4 shows the annual production of bioethylene and lignin, the revenues, and the economic indicators (IRR and VPN) for the selected capacity of 200 kt of industrial sawdust per year.

The analysis determined that more than 41 000 t of lignin and 21 421 t of bioethylene can be obtained with an NPV of about 5.21 MM USD using the selected assumption.

Risk and sensitivity analysis

Several factors were selected to determine their influence on the overall process. The most commonly used probability distributions are triangular, normal, and uniform. The adopted distributions resulted from a bibliographic collection. For more details, see Table S1.†

The sensitivity assessment results are shown in Fig. 6. The most influential variables are lignin and ethylene market

Table 3 Total capital investment

Concept	Factor	[MM USD] ^c
Purchased equipment		37.3
Installed cost	(1.2–2.75) ^b	30.4
Warehouse	(4%)	1.2
Site development	(9%)	2.7
Additional piping	(4.5%)	1.4
Total Direct Cost (TDC)		73.1
Proratable expenses	(10%)	7.3
Field expenses	(10%)	7.3
Home office and construction fee	(20% of TDC)	14.6
Project contingency	(10%)	7.3
Other cost	(10%)	7.3
Total indirect cost		43.8
Fixed Capital Investment (FCI) ^a		116.9
Land		1.0
Working capital investment	(10%) ^a	11.7
Total Capital Investment (TCI)		129.6
Lang factor (TCI/purchased equipment cost)		3.47

^a Factors estimated by the National Renewable Energy Laboratory (NREL). Parenthesis values correspond to % of the equipment cost.

^b Installing Factors are between 1.2–2.75, depending on the equipment.⁶⁶ ^c MM USD refers to millions of USD.

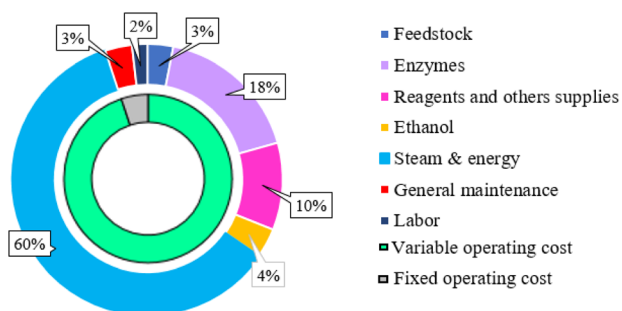


Fig. 5 Fixed and variable operating costs in the external circle. All costs are represented as a percent within the internal circle.

Table 4 Profitability analysis of multiproduct plant

Production capacity		
Lignin	41 572	t y ⁻¹
Bioethylene	21 421	t y ⁻¹
Revenue		
Lignin	37.41	MM USD y ⁻¹
Bioethylene	31.92	MM USD y ⁻¹
Profitability analysis		
Internal rate of return	10.08	%
Net present value	5.21	MM USD

price, followed by energy and enzyme costs. Regarding the technical factors, the pretreatment LSR and the available feedstock are the most relevant variables.

The availability of raw materials is also a critical factor that will be discussed in this paper. The most negligible influence on NPV is labour costs (operational, management, maintenance, administrative), sulphuric acid cost, and the ratio of washing water and water cost. With higher importance and in the same order, but not significant, are the cost of industrial sawdust and the steam economy.

Discussion

Future trends in the bioethylene and lignin markets

Until ten years ago, the production costs of bioethylene were higher compared with fossil-based ethylene (35%–65% depending on the feedstock and scale production).⁸⁰ However, during the last decade, the reduction in bioethanol prices per barrel⁸¹ has increased the competitiveness of biobased ethylene.^{82,83}

Future increases in fossil fuel prices and -potentially- in carbon pricing could make bioethylene production still more cost-competitive.^{84,85} Ethylene is a bulk chemical used primarily for polymer production, such as polyethylene. One kilogram of bio-polyethylene is around 30% more expensive than 1 kg of fossil-based polyethylene.⁸¹ However, this situation may change over time through research and development.

Bioethylene is also used for producing polystyrene (through the production of ethylbenzene), rubbers, epoxy resins, polyvinyl chloride, ethylene oxide, ethylene glycol through hydrolysis, and ethanol through hydration, depending on raw material prices. These applications represent a significant percentage of its production.^{81,86} Biodegradable plastics like polylactic acids, polyhydroxyalkanoates, starch blends, and others comprise over 51% (1.1 million tons) of global bioplastics production. Production projections indicate that it will reach around 3.5 million tons by 2027, propelled by the robust advancement of polymers.⁸⁷

In this study, we propose comprehensive biomass valorization to boost the economic performance of the proposed biorefinery. Given the increasing attention to high-purity lignin production and its diverse applications, we add this commodity to our product portfolio. The expansion can be attributed to incorporating natural constituents in manufacturing methodologies, offering promising avenues for advancing the lignin industry.^{88,89} We anticipate significant growth in the organosolv lignin segment due to its versatile applications, including serving as a filler in ink, paint, and varnish formulations, as well as in activated carbon, phenolic resins, carbon fibers, vanillin, phenolic derivatives, and concrete additives.^{89,90} Raw materials include straw, sugarcane bagasse, softwoods, and hardwoods, among others.^{90,91} Softwoods are particularly valuable in developing stabilized carbon fibers from lignin since their higher lignin content than hardwoods contributes to segment expansion.⁸⁸

Fig. 7 shows the market size projection for bioethylene and global lignin, distinguishing the segments representing low-purity and high-purity lignin.^{92–94}

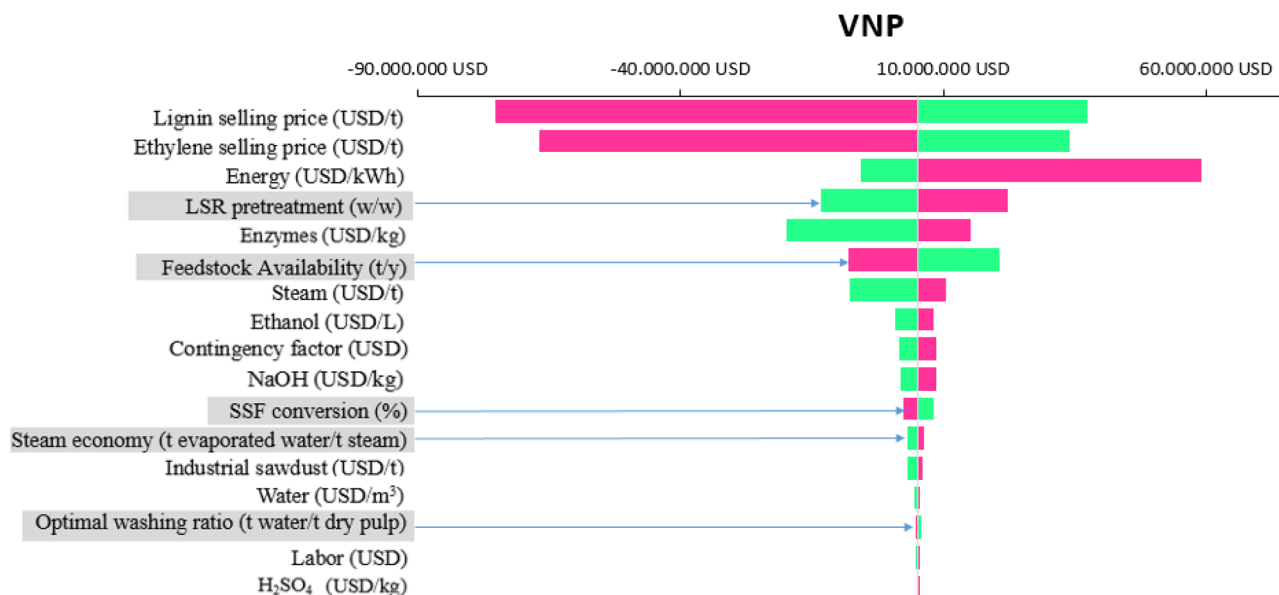


Fig. 6 Tornado charts for the selected variables. Technical factors are highlighted in gray color. Economic factors are not highlighted.

Market Size

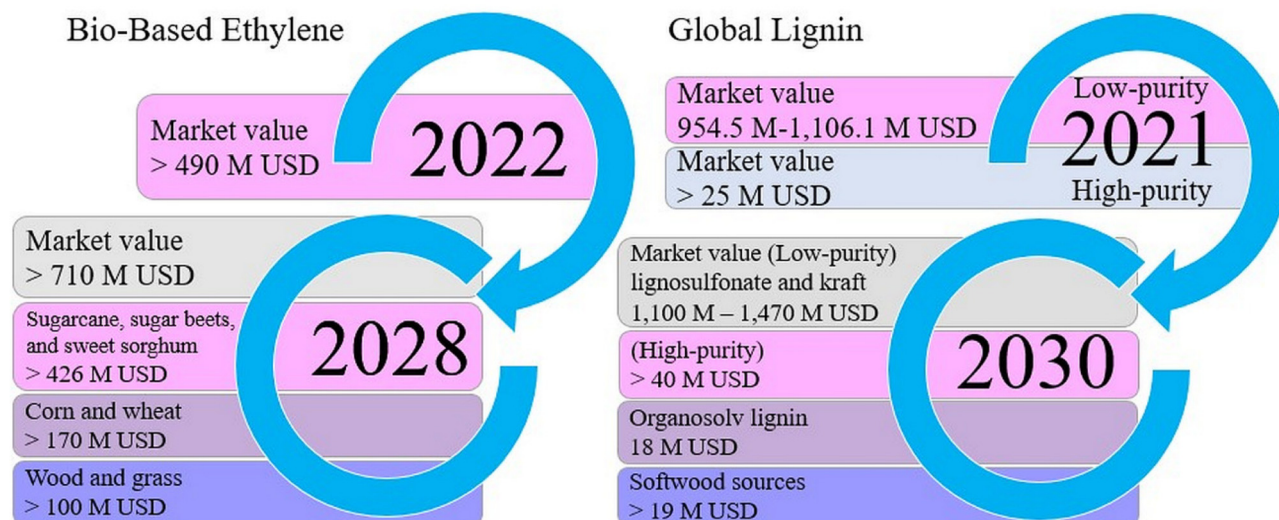


Fig. 7 Bioethylene and lignin market size.^{63,85,88,97,99,103–106}

The comprehensive global market valuation considers the presence of lower-purity lignin, which constitutes the predominant volume (with lignosulfonates comprising 80% of the total lignin market).⁹⁰

In addition, the combination of lignin-derived benzene and bioethylene has the potential to establish a biorefinery route for the synthesis of styrene (a market valued at 49 000 million globally in 2018, with a projected compound annual growth rate of 4.5% spanning from 2019 to 2025).⁹⁵

Key bioethylene and lignin manufacturers

The relevance of biobased product use and consumers' increasing positive attitudes and perceptions have driven companies toward plastics production and materials derived from renewable monomers.⁹⁵ Key bioethylene and lignin manufacturers are crucial players in the industry. They significantly influence the market dynamics and help shape the industry landscape.

Bioethylene companies are concentrating on increasing their production capacities and expanding their markets.

However, this market is emerging in The United States, Brazil, Canada, and a few European countries. Regarding bioethylene, Alberta holds a prominent position as a key manufacturer within the bioethylene market, and it is likely to invest heavily in research and development to enhance the efficiency and cost-effectiveness of bioethylene production processes. Their expansion approach might encompass collaborations with other companies, exploration of new markets, and capitalizing on technological advancements.

Similarly, Axens, a notable entity in the bioethylene sector, may prioritize innovating bioethylene production technologies to ensure product quality and sustainability.

Broadening global market presence through strategic partnerships and acquisitions could constitute a significant facet of their growth strategy.⁹⁶ Another established player is DowDuPont, which has substantial chemical industry expertise and might pursue expansion by leveraging their existing distribution networks to enter novel bioethylene markets.⁹⁷ Simultaneously, they could focus on sustainability initiatives and process optimization. Cargill, a significant contributor to the biobased chemicals domain, might execute a commercial expansion plan involving diversification of its product portfolio to cater to diverse industries and identify fresh applications for bioethylene. Collaborating with other industry leaders for joint ventures or partnerships might also be a pivotal element of their growth roadmap.^{85,98}

Lignin is a complex polymer of various phenylpropanoid aromatic building blocks with variable molecular weight distribution and chemical functionalities. These limit its valorization or processing into value-added products. Generally, lignin is used to obtain a pure product or formulations for a particular purpose, applying process groups to break lignin into small value-added molecules or using its polymeric structure for materials applications. In the last decade, the efforts of several companies to develop commercial processes for large-scale lignin manufacturing plants have been highlighted. Regarding lignin manufacturers, Suzano SA stands out as a chief producer with a robust market presence. Its strategic expansion plan could encompass increasing production capacity, ensuring consistent lignin quality, and exploring novel applications of lignin in industries such as construction, automotive, and packaging. Domtar Corporation prioritizes the sustainable sourcing of raw materials for lignin production and seeks collaborative opportunities to innovate new lignin-based products, thereby expanding its market reach through strategic partnerships.⁹⁹ West Fraser, a significant player, may focus on advancing technology for efficient lignin extraction and purification. Their commercial expansion strategy could involve venturing into emerging markets and fortifying distribution networks. Stora Enso's expansion approach may revolve around research and development investments for pioneering lignin-based products and applications.⁸⁸ Moreover, fostering partnerships with entities in the construction and chemical sectors could be instrumental in promoting the adoption of lignin-based products.^{100,101}

The chief manufacturers of bioethylene and lignin are likely to pursue diverse strategies to improve their competitiveness and shape the industry landscape. They may prioritize sustainability, technological advancements, product diversification, and strategic collaborations to drive growth and expand their market presence. The LSR used in the pretreatment is the most important technical factor. On an industrial scale, the lowest liquid–solid ratio is sought to have a smaller volume of liquid to heat and to be able to reduce the energy necessary to reach the pretreatment temperature.

Regarding energy integration, heat could still be used in other biorefinery processes. In addition, selling CO₂ from fermentation gases could be an option. Although highly pure, it can be further purified and marketed.⁹ A recent study reported that one ton of beech wood could produce polymer-grade bioethylene (15%), organosolv lignin (15%), biomethane (10%), and hydrolysis lignin (23%). However, they found that the heat-integrated biorefinery concept is not yet profitable and that the economic results significantly depend on the prices of beech wood, ethylene, and organosolv lignin.⁹

The prospects for both bioethylene and lignin exhibit considerable promise. Over time, there has been a discernible decline in the cost of cellulose-based raw materials, coinciding with a persistent escalation in crude oil prices. This trajectory was forecasted several decades ago and has indeed materialized with a remarkable level of certainty.¹⁰² Furthermore, industries are anticipating market share expansion, the formation of strategic alliances, heightened investments in research and development, and the strategic utilization of technological advancements.

Conclusions

This work presents a design of an industrial-scale biorefinery that has addressed the stages for its technical and economic development.

The evaluated process is an alternative to wood sawdust byproduct valorization on an industrial scale, obtaining bioethylene from the main line and lignin from the secondary line.

One of the main challenges in biorefinery design and development is uncertainty. It is necessary to apply sensitivity studies to delimit the range of factors affecting the technical and economic aspects variation, so a risk and sensitivity analysis was carried out considering various potentially critical factors.

The present value obtained in this study is 5.21 MM USD. However, the sensitivity analysis indicates that the maximum NPV could be close to 60 MM USD.

The selling prices of products, the cost of energy and enzymes, the pretreatment LSR, and the feedstock availability (in that order) resulted in the relevant factors of the study. A trend study of the critical factors would provide more information about this subject.

The steady growth of biobased products in the global market is attributed to the synergistic effects of supportive government policies, industry-driven initiatives, and a rising

demand fueled by heightened public awareness. This convergence of factors is driving the ongoing shift towards more sustainable and environmentally friendly product options.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The support of the National Scientific and Technical Research Council (CONICET) and the National University of Misiones (UNaM) are acknowledged.

References

- N. M. Clauser, F. E. Felissia, M. C. Area and M. E. Vallejos, *Renewable Sustainable Energy Rev.*, 2021, **139**, 1–17.
- M. C. Area and M. E. Vallejos, *Biorrefinería a partir de residuos lignocelulósicos, Conversión de residuos a productos de alto valor*, 2012.
- A. S. Nizami, M. Rehan, M. Waqas, M. Naqvi, O. K. M. Ouda, K. Shahzad, R. Miandad, M. Z. Khan, M. Syamsiro, I. M. I. Ismail and D. Pant, *Bioresour. Technol.*, 2017, **241**, 1101–1117.
- M. V. Mestre, *Ambienta*, 2018, **125**, 50–67.
- A. Uasuf and J. Hilbert, *El uso de la biomasa de Origen Forestal con destino a bioenergía en la Argentina*, Castelar, Buenos Aires, 2012.
- M. R. Bordón, G. Corsano and J. M. Montagna, *Actas de Jornadas y Eventos Académicos de UTN (AJEA)*, 2020, DOI: [10.33414/ajea.5.767.2020](https://doi.org/10.33414/ajea.5.767.2020).
- O. R. Calderon and V. Arantes, *Biotechnol. Biofuels*, 2019, **12**, 2–58.
- N. M. Clauser, PhD thesis, Universidad Nacional de Misiones, 2019.
- R. Nitzsche, M. Budzinski and A. Gröngröft, *Bioresour. Technol.*, 2016, **200**, 928–939.
- M. Frosi, A. Tripodi, F. Conte, G. Ramis, N. Mahinpey and I. Rossetti, *J. Ind. Eng. Chem.*, 2021, **104**, 272–285.
- A. Mohsenzadeh, A. Zamani and M. J. Taherzadeh, *ChemBioEng Rev.*, 2017, **4**, 75–91.
- S. Mesfun, L. Matsakas, U. Rova and P. Christakopoulos, *Energies*, 2019, **12**, 4206.
- N. Rajendran and J. Han, *Waste Manage.*, 2023, **156**, 168–176.
- D. Kumar, S. P. Long, A. Arora and V. Singh, *GCB Bioenergy*, 2021, **13**, 1498–1514.
- G. Barjoveanu, O.-A. Pătrăuțanu, C. Teodosiu and I. Volf, *Sci. Rep.*, 2020, **10**, 13632.
- P. Pérez-López, M. Montazeri, G. Feijoo, M. T. Moreira and M. J. Eckelman, *Sci. Total Environ.*, 2018, **626**, 762–775.
- J. Min-hee, Business Korea, <https://www.businesskorea.co.kr/news/articleView.html?idxno=32779>.
- I. D. Posen, P. Jaramillo and W. M. Griffin, *Environ. Sci. Technol.*, 2016, **50**, 2846–2858.
- A. López-Molina, D. Sengupta, S. Claire, E. Aldamigh, M. Alandejani and M. M. El-Halwagi, *Processes*, 2020, **8**(12), 1–18.
- E. A. Skiba, O. V. Baibakova, V. V. Budaeva, I. N. Pavlov, M. S. Vasilishin, E. I. Makarova, G. V. Sakovich, E. V. Ovchinnikova, S. P. Banzaraktsaeva, N. V. Vernikovskaya and V. A. Chumachenko, *Chem. Eng. J.*, 2017, **329**, 178–186.
- T. Kamsuwan, P. Praserttham and B. Jongsomjit, *Catal. Commun.*, 2020, **137**, 105941.
- D. Damayanti, D. Supriyadi, D. Amelia, D. R. Saputri, Y. L. L. Devi, W. A. Auriyani and H. S. Wu, *Polymers*, 2021, **13**, 2886.
- M. Broeren, Report-Production of Bio-ethylene, 2013, (<https://www.iea-etsap.org>).
- C. M. Mendieta, F. E. Felissia, A. M. Arismendy, J. Kruieniski and M. C. Area, *BioResources*, 2021, **16**, 7474–7491.
- C. Imlauer Vedoya, M. C. Area, N. Raffaeli and F. E. Felissia, *Sustainability*, 2022, **14**, 1–14.
- TAPPI, *Kraft pulping short course*, 1997.
- R. Valenzuela, X. Priebe, E. Troncoso, I. Ortega, C. Parra and J. Freer, *Ind. Crops Prod.*, 2016, **86**, 79–86.
- E. Araque, C. Parra, J. Freer, D. Contreras, J. Rodr, R. Mendonc and J. Baeza, *Enzyme Microb. Technol.*, 2008, **43**, 214–219.
- W. Wang and L. Tao, *Renewable Sustainable Energy Rev.*, 2016, **53**, 801–822.
- M. E. Vallejos, J. Kruieniski and M. C. Area, *Biofuel Res. J.*, 2017, **15**, 654–667.
- C. M. Mendieta, R. E. Cardozo, F. E. Felissia, N. M. Clauser, M. E. Vallejos and M. C. Area, *BioResources*, 2021, **16**, 4411–4437.
- Y. Hu, N. Zhan, C. Dou, H. Huang, Y. Han, D. Yu and Y. Hu, *Biotechnol. J.*, 2010, **5**, 1186–1191.
- I. Rossetti, M. Compagnoni, E. Finocchio, G. Ramis, A. Di, Y. Millot, S. Dzwigaj, A. Di Michele, Y. Millot and S. Dzwigaj, *Appl. Catal., B*, 2017, **210**, 407–420.
- Q. Sheng, K. Ling, Z. Li and L. Zhao, *Fuel Process. Technol.*, 2013, 2–3.
- A. Tripodi, M. Belotti and I. Rossetti, *ACS Sustainable Chem. Eng.*, 2019, **7**, 13333–13350.
- C.-Y. Wu and H.-S. Wu, *ACS Omega*, 2017, **2**, 4287–4296.
- I. M. S. Anekwe, M. Chetty, L. Khotseng, S. L. Kiambi, L. Maharaj, B. Oboirien and Y. M. Isa, *Catal. Commun.*, 2024, **186**, 106802.
- M. Díaz, E. Epelde, J. Valecillos, S. Izaddoust, A. T. Aguayo and J. Bilbao, *Appl. Catal., B*, 2021, **291**, 120076.
- M. Arvidsson and B. Lundin, Masters Thesis, Chalmers University of Technology., 2011, 1–113.
- P. Haro, P. Ollero and F. Trippe, *Fuel Process. Technol.*, 2013, **114**, 35–48.
- J. Bi, X. Guo, M. Liu and X. Wang, *Catal. Today*, 2010, **149**, 143–147.

- 42 M. A. Hubbe, R. Alén, M. Paleologou, M. Kannangara and J. Kihlman, *BioResources*, 2019, **14**, 2300–2351.
- 43 K. Nilsson, *Raising the efficiency of black liquor lignin extraction*, Lund University, Lund, Sweden, 2017.
- 44 E. K. Vakkilainen, *Recovery Boiler, Steam Generation from Biomass*, Elsevier, Butterworth-Heinemann, 2017, pp. 237–259.
- 45 A. García, M. G. Alriols, R. Llano-Ponte and J. Labidi, *Biomass Bioenergy*, 2011, **35**, 516–525.
- 46 A. Arkell, J. Olsson and O. Wallberg, *Chem. Eng. Res. Des.*, 2014, **92**, 1792–1800.
- 47 M. R. Olsson, E. Axelsson and T. Berntsson, *Nord. Pulp Pap. Res. J.*, 2006, **21**, 476–484.
- 48 M. Mahmoudkhani and D. W. Keith, *Int. J. Greenhouse Gas Control*, 2009, **3**, 376–384.
- 49 S. Kumar, P. Dheeran, S. P. Singh, I. M. Mishra and D. K. Adhikari, *Am. J. Microbiol. Res.*, 2013, **1**, 39–44.
- 50 W. Huang, *Energy Environ. Sci.*, 2011, **4**, 784–792.
- 51 L. M. Vane, *J. Chem. Technol. Biotechnol.*, 2005, **80**(6), 603–629.
- 52 J. Viell, A. Harwardt, J. Seiler and W. Marquardt, *Bioresour. Technol.*, 2013, **150**, 89–97.
- 53 C. Arato, E. K. Pye and G. Gjennestad, *Appl. Biochem. Biotechnol.*, 2005, 871–882.
- 54 S. Safarian and R. Unnthorsson, *Energies*, 2018, **11**, 1493.
- 55 G. Punter, D. Rickeard, J.-F. Larivé, R. Edwards, N. Mortimer, R. Horne, A. Bauen and J. Woods, *Well-to-Wheel Evaluation for Production of Ethanol from Wheat*, 2004.
- 56 P. Chongvatana, *Cooling System in Ethanol Plant with Starch Base Feedstock*, Ashrae Thail Chapter: 30–2. Available from: https://www.ashraethailand.org/download/ashraethailand_org/journal_2007-2008_35_coolingsystem.pdf.
- 57 M. Zhang and Y. Yu, *Ind. Eng. Chem. Res.*, 2013, **52**, 9505–9514.
- 58 N. M. Clauser, S. Gutiérrez, M. C. Area, F. E. Felissia and M. E. Vallejos, *Biofuels, Bioprod. Biorefining*, 2018, **12**, 997–1012.
- 59 *Ministerio de Agricultura Ganadería y Pesca, Dirección Nacional de Desarrollo Foresto Industrial, Relevamiento de las Industrias Forestales*, Argentina, 2020.
- 60 M. S. Acosta, C. Mastrandrea, C. de la Peña, L. Vergara, J. M. Roncaglia, L. Vianna, L. Vera and M. F. Palenzona, *Planilla de precios forestales*, 2021.
- 61 Secretaría de Energía, *Precios de Bioetanol, Presidencia de la Nación Argentina*, 2022.
- 62 D. de Guzmán, *R&D More Activities Open Up Lignin's Feedstock Potential*, forest2market, 2020.
- 63 J. Rajesh Banu, Preethi, S. Kavitha, V. K. Tyagi, M. Gunasekaran, O. P. Karthikeyan and G. Kumar, *Fuel*, 2021, **302**, 1–18.
- 64 G. Towler and R. Sinnott, *Chemical Engineering Design*, Elsevier, 2022, pp. 305–337.
- 65 P. R. Stuart and M. M. El-Halwagi, *Integrated Biorefineries, design, analysis and optimization*, CRC Press, United State of America, 1st edn, 2014.
- 66 J. Sadhukhan, K. S. Ng and E. Martinez, *Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis*, Wiley, United Kingdom, 1st edn, 2014.
- 67 J. Harmsen, *Industrial Process Scale-up: A Practical Innovation Guide from Idea to Commercial Implementation*, Elsevier, United Kingdom, 2013.
- 68 R. Davis, N. Grundl, M. J. Bidy, L. Tao, E. C. D. Tan, G. T. Beckham, D. Humbird, D. N. Thompson and M. S. Roni, *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update*, *Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Path*, 2018.
- 69 W. D. Seider, J. D. Seader and D. R. Lewin, *Product and Process Design Principles-Synthesis, Analysis, and Evaluation*, Wiley, 2nd edn, 2003.
- 70 S. S. da Silva and A. K. Chandel, *Biofuels in Brazil, Fundamental Aspects, Recent Developments, and Future Perspectives*, Springer, Sao Paulo, Brazil, 2014.
- 71 N. M. Clauser, F. E. Felissia, M. C. Area and M. E. Vallejos, *Chem. Eng. Res. Des.*, 2021, **167**, 1–14.
- 72 S. A. El-Temtamy and T. S. Gendy, *Egypt. J. Pet.*, 2014, **23**, 397–407.
- 73 A. K. Chandel, V. K. Garlapati, A. K. Singh, F. A. F. Antunes and S. S. Silva, *Bioresour. Technol.*, 2018, **264**, 370–381.
- 74 M. Mandegari, S. Farzad and J. F. Görgens, *Energy Convers. Manage.*, 2018, **165**, 76–91.
- 75 N. I. Vollmer, K. V. Gernaey and G. Sin, *Front. Chem. Eng.*, 2022, **4**, 1–18.
- 76 J. K. Ko, J. H. Lee, J. H. Jung and S.-M. Lee, *Renewable Sustainable Energy Rev.*, 2020, **134**, 110390.
- 77 H. J. Vázquez and O. Dacosta, *Ing., Invest. Tecnol.*, 2007, **8**, 249–259.
- 78 Y. Xu, L. Isom and M. A. Hanna, *Bioresour. Technol.*, 2010, **101**, 3311–3319.
- 79 T. Jarunglumert and C. Prommuak, *Fermentation*, 2021, **7**, 1–22.
- 80 J. McKechnie, M. Pourbafrani, B. A. Saville and H. L. MacLean, *Environ. Res. Lett.*, 2015, **10**, 124018.
- 81 S. S. Ali, E. A. Abdelkarim, T. Elsamahy, R. Al-Tohamy, F. Li, M. Kornaros, A. Zuurro, D. Zhu and J. Sun, *Environ. Sci. Ecotechnology*, 2023, **15**, 1–21.
- 82 V. Siracusa and I. Blanco, *Polymers*, 2020, **12**, 1641.
- 83 A. Teixeira Penteadó, G. Lovato, A. Pérez Ortiz, E. Esche, J. A. Domingues Rodrigues, H. R. Godini, A. Orjuela, J. Gušča and J.-U. Repke, *Processes*, 2021, **9**, 1–30.
- 84 A. Hasanbeigi and A. Sibal, *Deep Decarbonization Roadmap for the U.S. PVC Industry*, Florida, United States, 2023.
- 85 Precedence Research, <https://www.precedenceresearch.com/ethylene-market>, (accessed febrero 2024).
- 86 I. Rossetti, A. Tripodi and G. Ramis, *Int. J. Hydrogen Energy*, 2020, **45**, 10292–10303.
- 87 World plastics production 2021, Bioplastics market data, <https://european-bioplastics.org/market/>, (accessed 9 August 2023).

- 88 Global Market Insights, High Purity Lignin Market Size - By Product Type (Kraft Lignin, Organosolv), By Source (Hardwood, Softwood, Sugarcane Bagasse, Straw), By Application (Binders & Adhesives, Phenol, Vanillin, Carbon Fibre, Activated Carbon) & Forecast, 2022–2030, <https://www.gminsights.com/industry-analysis/high-purity-lignin-market>, (accessed 1 August 2023).
- 89 E. Hurmekoski, L. Hetemäki and J. Jänis, *Forest Bioeconomy an Climate Change*, ed. L. Hetemäki, J. Kangas and H. Peltola, Springer International Publishing, Cham, 2022, vol. 42, pp. 1–265.
- 90 L. Dessbesell, M. Paleologou, M. Leitch, R. Pulkki and C. Xu, *Renewable Sustainable Energy Rev.*, 2020, **123**, 109768.
- 91 M. Hassegawa, J. Van Brusselen, M. Cramm and P. J. Verkerk, *Land*, 2022, **11**, 2131.
- 92 D. S. Bajwa, G. Pourhashem, A. H. Ullah and S. G. Bajwa, *Ind. Crops Prod.*, 2019, **139**, 111526.
- 93 P. Sivagurunathan, T. Raj, C. S. Mohanta, S. Semwal, A. Satlewal, R. P. Gupta and R. Kumar, *Chemosphere*, 2021, **268**, 129326.
- 94 N. Mandlekar, A. Cayla, F. Rault, S. Giraud, F. Salaün, G. Malucelli and J.-P. Guan, *Lignin - Trends and Applications*, Intech, France, 2018, pp. 207–231.
- 95 E. Paone, T. Tabanelli and F. Mauriello, *Green Sustainable Chem.*, 2020, **24**, 1–6.
- 96 M. S. Reisch, *Chem. Eng. News*, 2019, **97**(42), <https://cendev.acs.org/business/biobased-chemicals/race-repurpose-garbage/97/i42>.
- 97 Bio-Based Ethylene Market Forecast to 2028 - COVID-19 Impact and Global Analysis By Raw Material (Sugars, Starch, and Lignocellulosic Biomass) and End-User Industry (Packaging, Detergents, Lubricant, and Additives), <https://www.theinsightpartners.com/reports/bio-based-ethylene-market>, (accessed 8 August 2023).
- 98 M. A. J. Sánchez, *Acta Univ. Multidiscip. Sci. J.*, 2020, **30**, DOI: [10.15174/au.2020.2654](https://doi.org/10.15174/au.2020.2654).
- 99 Market Analysis Report, Lignin Market Size, Share & Trends Analysis Report By Product (Lingo-sulfonates, Kraft Lignin, Organosolv Lignin, Others), By Application, By Region, And Segment Forecasts, 2023–2030, <https://www.grandviewresearch.com/>, (accessed 17 August 2023).
- 100 S. Mastrolitti, E. Borsella, A. Giuliano, M. T. Petrone, I. De Bari, R. J. A. Gosselink and H. Stichnothe, *Sustainable lignin valorization: Technical lignin, processes and market development*, 2021.
- 101 *Natural Polyphenols from Wood: Tannin and Lignin—An Industrial Perspective*, ed. K. Cheng and C. Hagiopol, Elsevier, Atlanta, 2021, pp. 123–145.
- 102 S. Osborne, *Energy in 2020: Assessing the Economic Effects of Commercialization of Cellulosic Ethanol*, Washington DC, 2007.
- 103 Green Chemicals, Lignin and Lignin-Based Products Market 2023 to 2030- Capacity, Production, Capacity Utilization Rate, Ex-Factory Price, Revenue, Demand & Supply, Import and Export, Cost, Gross Margin Analysis, <https://www.24chemicalresearch.com/>, (accessed 17 August 2023).
- 104 Markets and Markets, Ethylene Carbonate Market by Application (Lubricants, Lithium Battery Electrolyte, Plasticizers, Surface Coatings), End-Use Industry (Automotive, Oil & Gas, Industrial, Medical, Personal Care & Hygiene) and Region - Global Forecast to 2027, <https://www.marketsandmarkets.com/Market-Reports/ethylene-carbonate-market-229766138.html>, (accessed 7 August 2023).
- 105 J. Miller and M. Faleiros, *Lignin: Technology, Applications, and Markets*, 2016.
- 106 S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik and P. T. Anastas, *Green Chem.*, 2017, **19**, 1–31.