Deliverable report

D5.1 Full sustainability aspects (including LCA) of most promising lignin valorization chains

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Working Group 5

Introduction

Working group 5 intended to support the most promising lignin valorization chains via a multi-criteria evaluation of sustainability aspects. One of the main criteria was to assess process profitability so as to achieve maximal use of lignin's market potential and support its market deployment. During LignoCOST, the non-technical deployment barriers were identified and strategies in order to overcome them were assessed. Techno-economic, environmental and social aspects were evaluated to justify the utilisation of renewable resources for the production of bio-based products, as well as biorefinery development was applied for the improvement of the process efficiency and sustainability. Economic sustainability indicators were estimated to help convincing relevant stakeholders to focus on lignin valorization schemes. The potential development of large-scale production units, the evaluation of the time required to achieve technological maturity, market stability and expansion were also considered so as to compare the current status with the future potential and quantify the current gap for certain processes to reach the market performance. Finally, the policy and legislation amendments were assessed to facilitate industrial implementation of novel lignin valorization technologies.

Deliverable 5.1 will present the sustainability assessment of the most promising lignin valorisation value chains. A superstructure analysis approach has been followed to assess the techno-economic optimisation of the potential value chains. Moreover, the economic and environmental performance of lignin-based value chains has been assessed and compared with relevant fossil-based counterparts.

Methodology

Preliminary techno-economic evaluation (TEA)

The preliminary techno-economic methodology followed with accuracy up to ±30% has been described by Ioannidou et al. (2022). The industrial plant was assumed to operate 7920 h/y. Sizing of unit operations was performed based on standard engineering procedures described in the literature (Peters et al., 2003; Ulrich and Vasudevan, 2004; Turton et al., 2018). Fixed Capital Investment (FCI) was estimated by multiplying the sum of the free-on-board purchased equipment costs (Ceq.fob) with a Lang factor of 5 (Dheskali et al, 2020). The Lang factor ranges from 3 to 6 when the Ceq.fob is used for the estimation of the FCI (Peters et al., 2003; Turton et al., 2018). A Lang factor of 5 has been used due to the construction of a new industrial plant using a high-risk new technology and the utilization of expensive construction material in the process equipment.

The cost of manufacture (COM) was estimated using the equation proposed by Turton et al. (2018).

$$COM = 0.18 \times FCI + 2.73 \times C_{OL} + 1.23 \times (C_{UT} + C_{RM})$$

where C_{OL} represents the operating labour cost, C_{UT} includes utilities expenses and C_{RM} stands for the raw material expenses.

The coefficients used in equation 1 have been estimated by Turton et al. (2018) in order to include the contribution of all secondary product manufacturing cost categories (e.g. maintenance, marketing, R&D) that can be associated to the main cost categories used in equation 1. The unitary cost of utilities, supplied by off-sites, are $9.45/t low pressure steam (LPS), $0.0674/kWh for electricity and $0.0157/t cooling water

(Turton et al., 2018). The C_{UT} is estimated by multiplying the unitary cost of each utility with the utility requirements in each case. The methodology reported by Ulrich and Vasudevan (2004) has been employed to estimate the COL considering the workers per shift (N_{OL}) required for each plant operation, the total number of workers required in the industrial plant based on the annual plant operation (4.5), the working time of each worker (2080 h/year) and the average labour cost ($20/h).

Discounted cash flow (DCF) analysis has been carried out using the parameters reported by Humbird et al. (2011), namely 10% interest rate, 30 years plant lifetime, 100% equity financing, 7 years for depreciation based on the Modified Accelerated Cost Recovery System (MARS), 3 years plant construction period and working capital estimation as 5% of the FCI. The TEA indicators used are the Net Present Value (NPV), the Discounted Payback Period (DPP) and the Minimum Selling Price (MSP).

Life Cycle Assessment

Environmental life cycle assessment was carried out based on the LCA principles, a standardized methodology for the environmental assessment according to the ISO 14040 and 14044 standards (ISO, 2006). This framework includes four discrete but interdependent phases that must be followed when performing an LCA: definition of goal and scope, inventory analysis, impact assessment and interpretation of the results.

Goal and scope

The goal and scope phase describes the reason for the LCA performance, the target audience and the strategy that will be followed for reporting the final results. Some of the factors that should be defined in this stage to ensure LCA transparency and comparability are the functional unit of the study, the system boundaries of the process, the selected impact categories and related indicators, possible assumptions and foreseeing uncertainties from uncontainable factors of the system and, possibly, the relevant perspective of the study, e.g. whether the LCA is attributional or consequential. The FU is employed to establish a reference to which the final impacts are expressed. Systems that provide significantly diverse products, yet meet the same requirement, can be compared using the same FU. The functional unit could be linked to a quantity of required product (output-based FU) or to the quantity of the feedstock under valorisation (input-based FU).

Life Cycle Inventory (LCI)

During the life cycle inventory phase (LCI), data for consumption of resources and utilities are collected as well as the quantities of waste flows and emissions caused in each stage of production are estimated. The analysis investigates all of the processes that are part of the product system, and the flows are scaled in line with the product reference flow provided by the functional unit. As most product systems are comprehensive, inventory analysis frequently relies on data that are derived from databases with unit processes or cradle-to-gate data, presenting the input and output flows for one unit process, such as material production, heat or electricity generation, transportation or waste management. This stage results in the development of the life cycle inventory, which is a list of quantified physical elementary flows for the product system expressed on the basis of the FU. This inventory is subsequently employed for the assessment of the environmental performance of the system under study.

Life Cycle Impact Assessment (LCIA)

The evaluation and quantification of the potential environmental impacts of the process is performed in the impact assessment phase by analyzing the data of the LCI. This phase provides indicators, in terms of several impacts categories, to evaluate the product life cycle on the selected FU basis considering the contributions of all the stages of the production process (Singh et al., 2018). For the cases under study, the LCA was carried out using the CML 2001 (Jan. 2016) methodology, as the most cited methodology for environmental assessment (Guinée et al., 2002; Ioannidou et al., 2020), while the LCA software GaBi was used for the

estimation of environmental indicators. The final results are expressed using the quantitative indicators most frequently used in literature, namely Global Warming Potential (GWP) and Abiotic Depletion Potential (ADP fossil) (Ioannidou et al., 2020).

Interpretation

Life cycle interpretation should occur at every stage in an LCA but more systematically when obtaining life cycle inventory and impact assessment results. The results of the study are interpreted in order to answer the questions posed in the goal and scope phase. Moreover, conclusions are drawn, the limitation of the LCA study are defined based on the main results and the selected comparisons and recommendations are provided for further elaboration.

Case studies

1. Process superstructure optimization for resins and aromatic monomer production from Kraft Lignin

Two different potential products derived from lignin, namely aromatic monomers (AMs) and PFRs, were considered by several alternative process routes (Figure 1). A simplified approach based on mixed-integer nonlinear programming (MINLP) is presented and applied to find the optimal Kraft lignin allocation to products and the optimal relevant processes aiming at an economic objective function. In particular, a sensitivity analysis on product selling prices was performed; in this way, the minimum selling price of the optimal product was identified, comparing it with the minimum selling price to make convenient the other product.

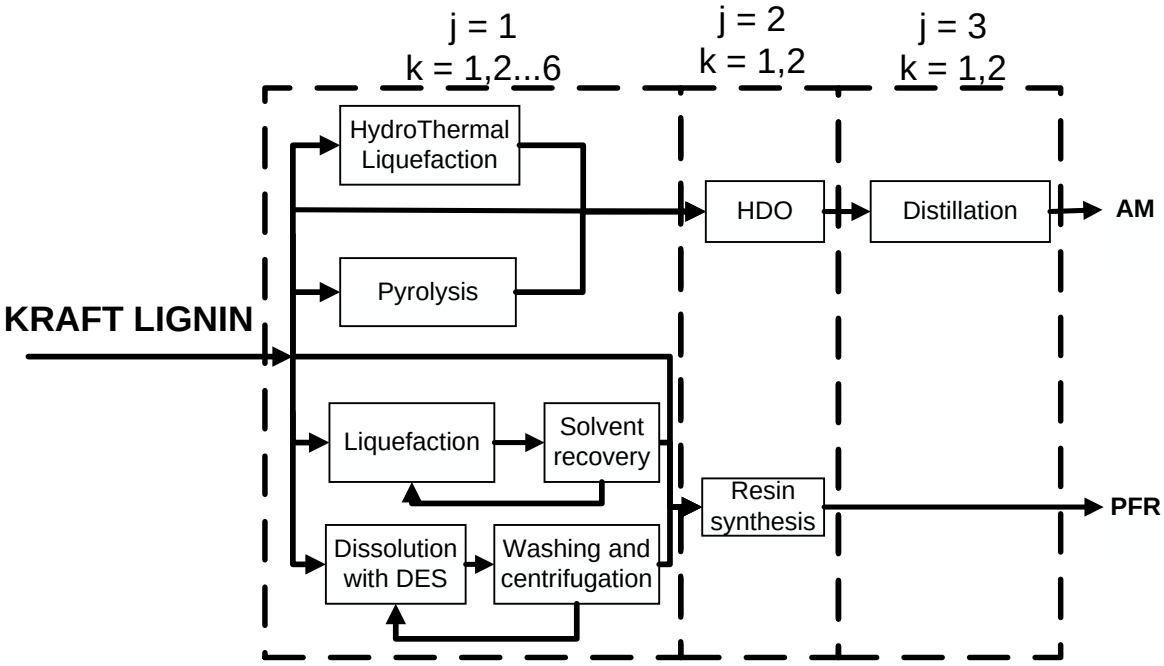


Figure 1: Superstructure of the proposed Kraft lignin-based biorefinery

1.1 Description of the superstructure

The optimization problem consists of finding the optimal process flowsheet and the optimal feedstock allocation to products for a lignin-based biorefinery, given an objective function (Giuliano et al., 2014). For this aim, the process pathways were included in a superstructure with different processing steps organized

in three layers (Galanopoulos et al., 2019). On the first layer, there are three different sections *j*: pretreatment, synthesis, and purification. Each section includes up to six alternative operations *k* (second layer) and each operation consists of up to 2 different process units *p* (third layer). After optimization, each layer *j* is restricted to only one operation option *k*. The lignin-based biorefinery optimisation problem aims at deciding which route to take through the network and the relevant flows entering and leaving each layer in order to maximize the maximum lignin cost, *MLC*. The latter *MLC* was derived as the maximum cost of dry lignin allowing a positive net profit from the biorefinery operations:

$$MLC = \max c_L \tag{1}$$

To set the economic analysis, the following constraints were considered:

$$\begin{cases} NetProfit = F_{3,AM}p_{AM} + F_{3,PFR}p_{PFR} - TAC - AIC = 0 \\ TAC = RMC + WWC + UTC + OMC \\ RMC = F_a c_a + F_{IN,L} c_L \end{cases} \tag{2}$$

where $F_{3,AM}$ and $F_{3,PFR}$ denotes the flowrate of AMs and PFRs, respectively, p_{AM}, p_{PFR} the product selling prices, TAC the total annual costs, AIC the annualized investment costs, RMC the raw material costs, WWC the wastewater treatment costs, UTC the utilities costs, OMC the operating & maintenance costs, F_a the auxiliaries material flow rates, c_a the chemicals/auxiliaries costs (listed in Table 1), and $F_{IN,L}$ the dry lignin feedstock flow rate.

The AIC calculation for each process operation k was performed by means of power law functions of the input flow rate. In particular, the parameters for the calculation of capital cost were obtained from Hamelinck et al. (2005). The annualization factor was set up as in the work of Galanopoulos et al. (2019). To consider the Kraft lignin as a complex material composed of fragments with different molecular weights, reactivities and functional groups, a percentage by weight of the whole dry lignin was assumed to be reactive in conversion processes.

A superstructure of the lignin-based biorefinery was built with the most commonly used pathways according to an accurate literature survey. In particular, it consists of six lignin pretreatment routes, two product synthesis processes and two purification operations, which can be summarised as follows:
j=1; k=1: the hydrothermal upgrading is used to convert lignin to monomers by depolymerisation. Water/NaOH solution at a medium temperature (200–350 °C) and high pressure (>40 bar) with a liquid-to-solid ratio of 5 kg/kg is considered to dissolve lignin. The reactor performance on the available lignin is assumed according to Gursel et al. (2019) findings;
j=1; k=2: the dry lignin is sent directly to the hydrodeoxygenation (HDO) reactor. In this case, a lower AM yield in the HDO can be obtained;

Table 1: Chemicals, solvents, reactants costs considered in the economic analysis

Component	Section of the superstructure	Cost
	j, *k*	€/kg
Hydrogen	2, 1	2.00
Ethanol	1, 5	0.50
DES	1, 6	0.80
H_2SO_4	1, 1	0.08
NaOH	1, 1	0.15
Formaldehyde	2, 2	0.60

j=1; k=3: the thermochemical process of pyrolysis is used to break down lignin, by means of heat and in the absence of oxygen, to obtain the aromatics (Gursel et al., 2019);
j=1; k=4: the dry lignin is sent directly towards the synthesis of PFRs (Kalami et al., 2017). Without the pretreatment, low molecular weight lignin can be effectively converted to resins;
j=1; k=5: a bio-crude oil is produced by the hydrothermal liquefaction process. Lignin is sent to the reactor with a water-ethanol (1:1 v/v) solvent. The reactor is operated at 350 °C and 20 bar (Paysepar et al., 2020);
j=1; k=6: a Zn-based deep eutectic solvent (DES) is used to dissolve and transform the lignin by a low-energy process (100 °C). Polyphenols in solution can be incorporated into the next PFRs synthesis (Hong et al., 2020);
j=2; k=1: HDO process is the main process step to produce the AMs from lignin. A mixed oxygenated aromatic monomers stream is obtained at 400 °C and 150 bar with a percentage of hydrogen equal to 3 wt% (Shen et al., 2019);
j=2; k=2: resin synthesis is performed by mixtures of lignin-water-NaOH-formaldehyde at 80 °C (Paysepar et al., 2020);
j=3; k=1: a distillation train is used in order to purify the AMs. First, the light organics are separated by distillation due to their lower boiling point. A second distillation column is used to separate water from the other components. Finally, AMs are completely separated from the high-boiling heavy organics in a third distillation column.
j=3; k=2: a purification process for PFRs is not necessary.

The model parameters used in this work is given in Table 2. The size of the biorefinery is an essential parameter to make the plants convenient and environmentally sustainable (Galanopoulos et al., 2020). Considering the possibility of collecting the feedstock in a limited area, e.g. near a paper mill, the input flow rate to the plant was assumed to be 180,000 t/y of dry Kraft lignin.

1.2 Results

The results of this work consist in the MLC value which makes the biorefinery economically viable. Values of *MLC* lower than €50/t are considered too low (Giuliano et al., 2020), as the cost of producing/processing the feedstock to make it suitable for pretreatment can be high. Other economic results consist in the capital costs to build the lignin valorisation biorefinery. Capital costs higher than M€150 for about 200,000 t/y of feedstock are considered too expensive due to being higher than capital costs of a lignocellulosic biorefinery producing bioethanol (Chemicals-technology, 2020). The operating costs play the main role, as the consumption of utilities (especially medium-pressure steam), the consumption of chemicals or solvents (even if solvent recycling were considered) can vary depending on the process pathways.

Table 2. Economic and process parameters used in the superstructure optimisation model.

Model parameter	Value
Dry lignin feedstock (t/y)	180,000
Yearly operation time (h)	7200
EtOH/Lignin	6.1
DES/Lignin	10
Discount rate (%)	8
Maintenance & operating/capital costs (%)	10
Wastewater purification cost (€/t)	0.53
Electricity cost (€/MWhe)	150
Lifetime (y)	20

In order to evaluate the impact on the optimisation of two main economic parameters, a sensitivity analysis varying the selling prices of PFRs and AMs was performed. The base price of AM, assumed equal to €1.20/kg (Shen et al., 2019), was increased and decreasing by 50%. Because of the different final performance of resins is difficult to evaluate in the present analysis, the PFR selling price was varied in a wider range between €0.10/kg and €1.00/kg. Figure 2 reports *MLC*, *CC* and *OC* as a function of the AM price and PFR price. The main expected result consists in a general decrease of the *MLC* with decreasing p_{PFR}. In particular, for the case of p_{AM}= €0.60/kg a minimum value of p_{PFR} equal to €0.40/kg is necessary to obtain a non-negative *MLC* value. For p_{PFR}>€0.60/kg the optimal product is always the PFR, whatever is the AM price in the investigated range. For higher values of p_{AM} (€1.20/kg and €1.8/kg) a threshold value for p_{PFR} is observed, below which the *MLC* value remains constant and positive. In particular, for p_{AM} equal to €1.20/kg, AM is the optimal product only for p_{PFR} <€0.40/kg with a very low *MLC* (about €12/t). For p_{AM} equal to €1.80/kg, AM is the optimal product for p_{PFR} < €0.60/kg, with a higher *MLC* (€196/t). Capital costs are not very variable with the product prices since the same process path leads to the same capital costs. In particular, when AM are produced, the process with hydrothermal upgrading is to be preferred, with investment costs of M€155. When PFR is the optimal product, liquefaction results the preferred pre-treatment process at low p_{PFR} values, while dissolution with DES (Deep Eutectic Solvents) arises for high p_{PFR} values (>€0.80/kg). In the latter case the capital costs are higher and equal to M€181. In fact, obtaining a higher yield to PFR by means of the more expensive pretreatment with DES is justified by the higher PFR selling price. Operating costs follow a similar variation with the product prices. In the case of AM production, the *OC* amount to about M€50/y, mainly due to the hydrogen consumption and utilities. In the case of PFR production, when liquefaction is the optimal pre-treatment, the *OC* are equal to M€15/y due to the consumption of formaldehyde. Differently, they increase up to M€84/y due to the DES make-up cost.

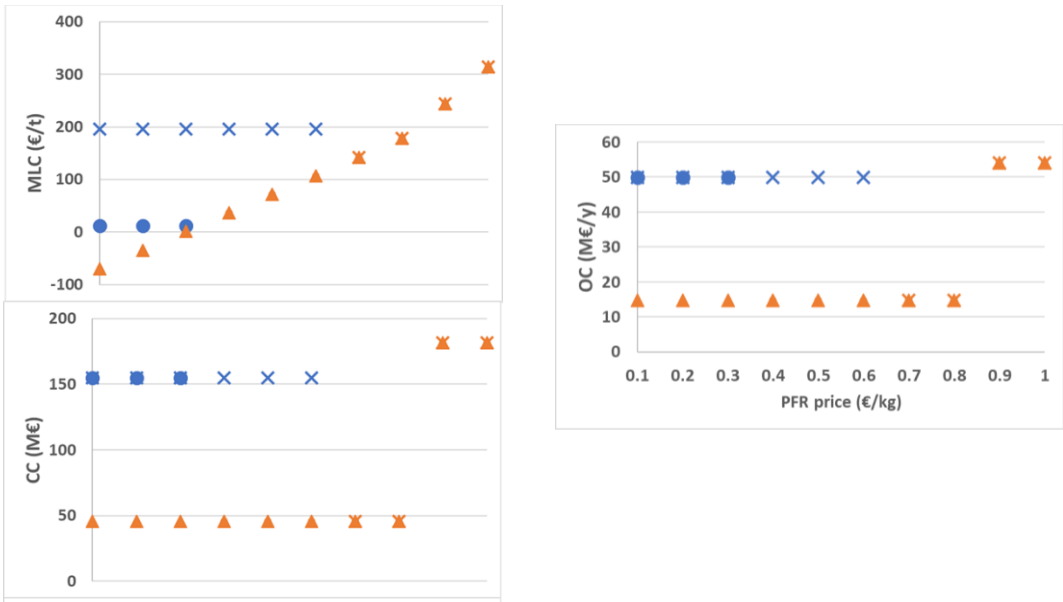


Figure 2: Maximum lignin cost (MLC), capital costs (CC), operating costs (OC) as a function of the PFR and parametric in the AM selling price: ▲ €0.60/kg; ● €1.20/kg; ✕ €1.80/kg. Blue symbols correspond to AM as the optimal product, and orange symbols correspond to PFR as the optimal product.

2. Techno-economic optimization of a process superstructure for lignin valorization

In this work, the main goal was to compare different process layouts for the valorization of different technical lignins and to assess economic indexes driving the analysis of the most profitable scenario. Different process designs are included based on commercial/pilot scale conversion processes available in the literature. Sensitivity analyses were performed on the most prominent parameters.

The novelty of the present work lies in applying an integrated optimization method to assess the most efficient lignin route to aromatic monomers (AM), phenols-formaldehyde resins (PFR), and aromatic aldehydes/acids (AA). A process superstructure incorporating alternative processes for the three products above-mentioned is treated in detail in this work as there are no previous works in literature addressing a simultaneous comparison of the profitability of various lignin valorization technologies. The process flowsheet optimization of a lignin-based biorefinery was addressed by mixed-integer non-linear programming (MINLP), aiming at an economic objective function. The effect of the product selling price of AM, PFR, and AA was assessed through a scenario analysis. Three different scenarios were considered: the first assuming the current products' selling price; the second, considering a lower AA selling price; the third, assuming a high AM selling price. A breakdown of the costs for each scenario was examined and addressed.

A novel methodology that formulates each process operation as a mathematical formulation has been implemented in this work to achieve the process optimization for lignin conversion by simultaneously evaluating every technology included in the superstructure. The state of art for each conversion process was studied to collect all available data in terms of yields, temperature and pressure conditions, reactants and solvent concentrations, products market prices. The next step was a conceptual process design followed by process model development. The various routes were represented in a flowsheets with the data collected from a detailed literature survey. Each block in the superstructure translates in mass and energy balances. Sizing relationships and process conditions constraints were determined. The superstructure was modelled using the Advanced Interactive Multidimensional Modeling System (AIMMS) software as a mixed integer non-linear model to maximize the maximum lignin market price (MLMP). Economic analysis methods were applied using the data collected in order to calculate the capital and operating cost. Finally, to identify the profitable pathways, a sensitivity analysis with an economic objective was performed.

As an overview, technical lignins include:

- Kraft lignin (KL), obtained through the acid precipitation process of the black liquor, presents a MW in the range of 1000–5000 (g/mol). Sulfonate groups are absent, and the most abundant functional groups are methoxy groups with percentage values in the range of 11–14%. Non-hindered methoxy groups are responsible for their great potential use in the synthesis of phenolic resins (Mastrolitti et al., 2021).
- Lignosulfonates (LS), from the sulfite pulping process, SO_3H groups are incorporated on the lignin structure producing a water-soluble lignin derivative (Laurichesse and Avérous, 2014);
- Soda lignin (SL), results from the soda pulping method isolation and presents a molecular weight range between 840 and 6820 Da; they are suitable to use in high-value products as it contains no sulfur (Azadi et al., 2013);
- Organosolv lignin (OL), presents a range of low molecular weights. OL is soluble in basic solutions, and β-O-4 ethers are targeted during isolation. Consequently, they are considered an apt raw material to produce low molecular weight compounds and for the production of polymers, such as bio-based PFR, polyurethanes, and polyesters (Dornelles et al., 2021);
- Steam-explosion lignin (SEL), is obtained when biomass is put through steam explosion isolation (Constant et al., 2015);
- Other types of lignins consist of milled wood lignin (MWL), hydrolysis lignin (HL), and ionic liquid lignin (Cao et al., 2019).

In Figure 3, a representation of the different lignin valorization techniques is depicted, showing their main highlights and challenges. The three processes on the left: hydrothermal liquefaction, pyrolysis, and oxidative depolymerization, are already established technologies operating on a commercial scale but present the disadvantage of low yields. The catalytic upgrading, hydrodeoxygenation (HDO), and catalytic oxidative depolymerization, on the other hand, are catalyzed technologies that have the advantage of being highly selective as well as flexible operations. On the right are the innovative operations developed on a pilot scale, HTE and DES dissolution; they have higher yields but with the challenge of higher costs. When converting lignin into valuable bio-based products, the main challenge is to develop novel processes that can perform the conversion in a selective, efficient, and sustainable way. To identify the most suitable pathways that increase the profitability of the various operations under consideration, process synthesis integration and optimization can be used (Giuliano et al., 2014).

2.1 Description of the superstructure

A superstructure is a conceptual model including alternative process pathways that can be converted into a mathematical model with an objective function and a set of constraints. Using a MINLP approach and by selecting the most promising alternative processes from a rigorous literature examination, the superstructure of a lignin-based biorefinery was built (Fig. 4) (Ramos et al., 2019). Table 3 shows a description of each process considered in the different stages of each lignin-based target product. Data input, such as yield factors and operating conditions, was obtained from several specific scientific references (Abdelaziz et al., 2020; Gursel et al., 2019; Hong et al., 2020; Kalami et al., 2017; Walch et al., 2021). There are three different stages j (Main treatment, Upgrading and Purification) including up to nine different technology options k, each one consisting of two different operation parts p. The mass and energy balance equations, sizing equations, capital and operating cost estimation equations, together an economic profitability objective function were considered. The concept of lignin reactivity was introduced to have a simplified qualitative index somehow accounting for the wide variability of the lignin characteristics and quality. The molecular weight distribution, the complex composition of the material (H/S/G ratios), the different types of bonds (β-O-4, β-β, etc.), and impurities, all affect the fraction of lignin reacting to give the target products. In the present investigation, various lignin sources were modeled varying their reactivity in the range of 50 – 95%, to be converted into three lignin-based target products.

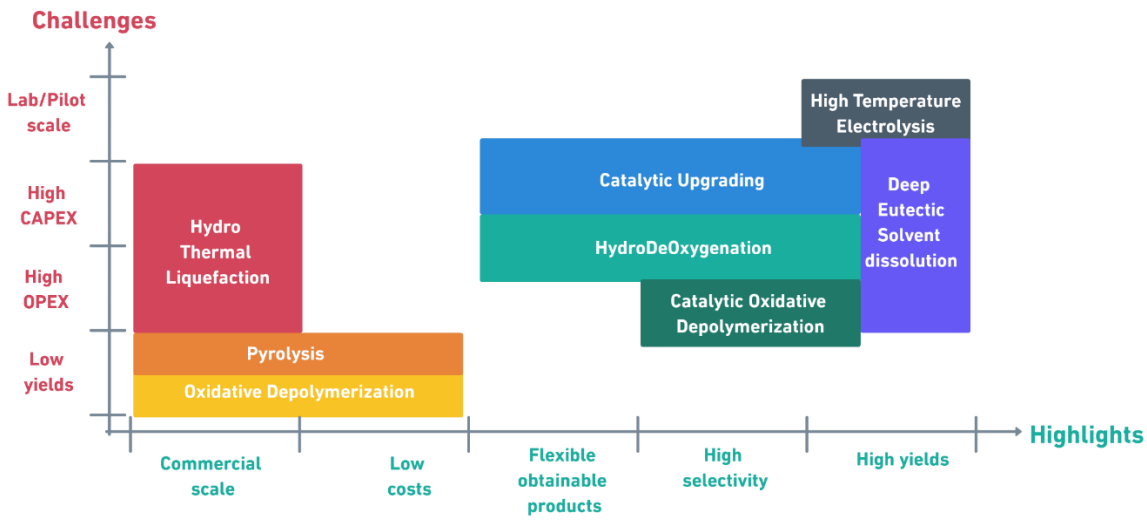


Figure 3. Different lignin valorization techniques and their main highlights and challenges.

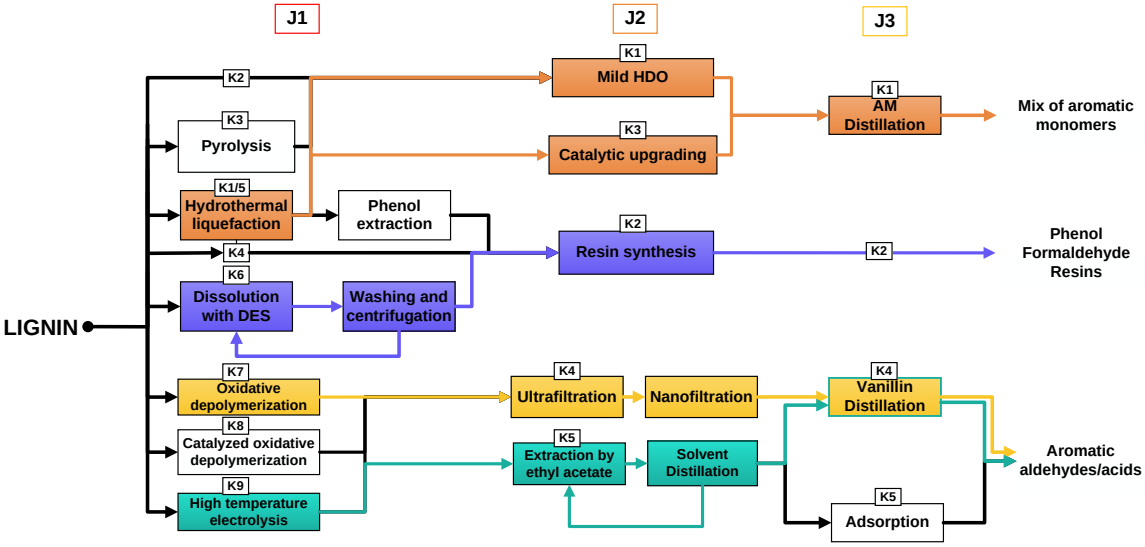


Figure 4. Optimal flowsheets obtained from the superstructure by maximizing the objective function.

Table 3. Process stages description for each lignin-based target product

j	k	Product	Process description	Reference
1	1	AM	Hydrothermal upgrading: lignin into monomers by depolymerization; 200–350 °C; >40 bar	(Gursel et al., 2019)
1	2	AM	Dry lignin is sent directly to the HDO reactor	(Gursel et al., 2019)
1	3	AM	Pyrolysis: break down lignin; heat and absence of O_2	(Gursel et al., 2019)
2	1	AM	HDO: as an upgrading process to transform lignin bio-oil to AM	(Shen et al., 2019)
3	1	AM	distillation train	(Kalami et al., 2017)
1	4	PFR	Dry lignin is sent directly to the PFR synthesis	(Kalami et al., 2017)
1	5	PFR	Hydrothermal liquefaction: production of bio-crude oil for the following PFR synthesis	(Paysepar et al., 2020)
1	6	PFR	DES: dissolution and transformation of lignin to polyphenols	(Hong et al., 2020)
2	2	PFR	Resin synthesis performed by mixtures of lignin-water-NaOH-formaldehyde	(Paysepar et al., 2020)
3	2	PFR	PFR purification not necessary	(Paysepar et al., 2021)
1	7	AA	Oxidative depolymerization of lignin	(Abdelaziz et al., 2020)
1	8	AA	Oxidative depolymerization of lignin catalyzed by homogeneous catalyst V–Cu (V/Cu 0.75)	(Walch et al., 2021)
1	9	AA	HTE of lignin	(Zirbes et al., 2020)
2	5	AA	Liquid-liquid extraction by ethyl acetate	(Khwanjaisakun et al., 2020)
2	4	AA	Membrane sets recover unreacted lignin as retentate; organic compounds are separated from the aqueous stream by a hydrophobic membrane	(Abdelaziz et al., 2020)
3	4	AA	The first column removes organic fraction from water; at 185 °C; 10 bar. In the second column, formic and acetic acid are separated weight aromatic products into two Distillation columns	(Abdelaziz et al., 2020)
3	5	AA	Adsorption by resins	(Wang et al., 2013)

2.2 Lignin to aromatic monomers

In particular, the first strategy constitute an alternative to fossil fuel-derived chemicals. This strategy involves depolymerization of the lignin through either catalytic or non-catalytic thermochemical conversion to produce low molecular weight chemicals with higher added value. Hydrothermal upgrading is used to convert lignin into monomers by depolymerization. The reactor performance is assumed to be as reported by Gursel et al. (2019). Alternatively, the dry lignin is sent directly to the HDO reactor. In which case, lower yields to AM can be obtained in the HDO. Additionally, the thermochemical process of pyrolysis is used to break down lignin, utilizing heat and in the absence of O_2, to obtain the aromatics (Gursel et al., 2019). HDO was also considered as an upgrading process to transform the lignin-derived bio-oil to AM. In this case, obtaining a mixed oxygenated AM stream at 400 °C and 150 bar with a 3 wt% of H_2 (Shen et al., 2019). Next, a distillation train is used to purify the AM. First, a distillation unit separate the light organics, with lower boiling point. A second unit of distillation is used to separate water from the other components. The separation of AM from high-boiling heavy organics is completed in the third distillation column.

2.3 Lignin to phenol-formaldehyde resins

The second strategy uses lignin as a macromolecular compound for formaldehyde-free applications. Lignin selective functionalization improves affinity and performance in resins, composites, and co-polymer materials (Kalami et al., 2017). In this case, the dry lignin is sent directly to the PFR synthesis (Kalami et al., 2017). Without the pretreatment, the lower molecular weight lignin can be effectively converted to resins. Moreover, in the PFR process pathway, a bio-crude oil is produced by the hydrothermal liquefaction process where lignin is sent to the reactor with a water-ethanol (1:1 v/v) solvent. The reactor is operated at 350 °C and 20 bar (Paysepar et al., 2020). DES can be used to dissolve and transform the lignocellulosic biomass, and in the specific, the lignin (Procentese et al., 2015) . This innovative technology results convenient in virtue of its high performances and simplicity to be recycled, by centrifugation and precipitation processes. Various solvents can be used, each one with specific characteristics and advantages, such as the structural properties of choline chloride (ChCl):lactic acid (Satlewal et al., 2019) high performances at mild temperature of ChCl:oxalic acid (Satlewal et al., 2018) or demethoxylation oriented performances of $ZnCl_2$/acetamide at low temperature (100°C) (Hong et al., 2020). In particular, a low-energy process using Zn-based DES was considered in this work. Subsequently, polyphenols in a solution can be incorporated into the next PFR synthesis (Hong et al., 2020). Finally, the synthesis of the resins is performed by mixtures of lignin-water-NaOH-formaldehyde at 85°C (Paysepar et al., 2020).

2.4 Lignin to aromatic aldehydes

The third target product is vanillin; 99% of the produced vanillin originates from petroleum (Zevallos Torres et al., 2020). With a market price of about €15/kg, vanillin is the only lignin-derived product that can currently compete with the vanillin obtained from fossil sources (Hodásová et al., 2015). The process described by Wongtanyawat et al. (2018) was taken as the base case for the production of specific aromatic compounds. Vanillin production by oxidative depolymerization of industrial lignin is reported by Abdelaziz et al. (2020), where experimental data for the KL treatment with air at 160 °C and 3 bar O_2 partial pressure are available.

The second process to produce vanillin is catalyzed oxidative depolymerization. This consists of treating lignin with molecular O_2 at 170 °C and 5 bar O_2 partial pressure with a bio-crude oil produced with V–Cu (V/Cu ratio 0.75) as a homogeneous catalyst (Walch et al., 2021). The novel process of high-temperature electrolysis (the) was performed with Ni foam electrodes (applying 2.7 C per mg lignin) dispersed in a 3 M aqueous caustic soda solution at 160 °C (Zirbes et al., 2020). From lignin conversion into vanillin, other aromatics such as vanillic acid, acetovanillone, syringaldehyde and p-hydroxybenzaldehyde can be obtained.

Khwanjaisakun et al. (2020) studied three alternatives to find the optimal vanillin purification flowsheet, concluding the liquid-liquid extraction with solvent and vanillin recovery by distillation Thus, this upgrading alternative was added to the superstructure along with the membrane separation option proposed by Abdelaziz et al. (2020). Pulping production companies use a great amount of toxic solvents, such as toluene and benzene, for liquid-liquid extractions. Werhan (2013) revealed that ethyl acetate is an effective solvent to extract vanillin as it presents a high recovery of this component. In particular, a liquid-liquid extraction by ethyl acetate at 62 °C was considered. The solvent was recovered by distillation at 160 °C and 0.13 bar (Khwanjaisakun et al., 2020). Alternatively, the vanillin-rich mixture is sent from the transformation stage to a first membrane filtration unit operating at 50 °C and 7.5 bar, where the retentate stream containing the recovered unreacted lignin is obtained. On the other side, the permeate is sent to another hydrophobic membrane (50 °C, 10.2 bar) that removes the organics from the aqueous stream, selectively (Abdelaziz et al., 2020).

For the final purification of vanillin, two alternative processes were considered: distillation and adsorption. After the upgrading section, where the remotion of sulfuric acid is performed in an extraction unit that uses ethyl acetate as a solvent or by a filtration executed by two membranes in series, the AA product are finally separated by distillation or adsorption. In Wongtanyawat et al. (2018), particular focus was put on the use of different product separation techniques revealing that the production of vanillin from Kraft lignin using adsorption by zeolite is the most promising option. Werhan, 2013 concluded that the use of cationic ion exchange resins for vanillin recovery is a potential process step for vanillin production from lignin-related sources.

The stream coming from the upgrading section is submitted to two distillation columns in series. The remaining organic fraction is purified at 185 °C and 10 bar by the first one and sent to the second distillation column (operating at 30 °C and 2.5 bar) in which formic acid and acetic acid are recovered from the low molecular weight aromatic products (Abdelaziz et al., 2020). In the adsorption section, operating at pH 4.5 and 40 °C, resins can adsorb the mixed products (Wang et al., 2013). In addition, unconverted lignin and water were also obtained as outputs.

The above-mentioned alternative processes were included in a complex process flowsheet to create the so-called superstructure of a lignin biorefinery for the co-production of AM, PFR, and AA. The whole superstructure built for this study is shown in Fig. 4.

2.5 Results

In order to establish the economic feasibility of a plant that acquires lignin as feedstock from the market, an economic objective function to be maximized was chosen. Maximum Lignin Market Price (MLMP) is defined as the maximum cost of dry lignin allowing a positive or null net profit from the biorefinery operations (as a netback). The present work focuses on determining the MLMP outlined for different product-selling-price scenarios. When considering a certain process pathway and a market price scenario, the MLMP resulting from the use of a specific lignin source must be above the minimum market value of the same lignin type for the process to be profitable. Contrarily, the use of that technical lignin as a feedstock will not yield any benefits.

Firstly, a “current scenario” (Cs) was determined considering the current market selling prices of AM, AA, and PFR (€1.00/kg, €15/kg and €0.80/kg, respectively). The second framework considered the “low AA price scenario” (LAAs) and assumed a disadvantageous case for AA in which their price was reduced by 50% (to €7.5/kg) compared to the current selling price. This hypothesis is based on the fact that the selling prices of vanillin (and its aldehydes) would decrease drastically in case of an overproduction of these products. Lastly, the “high AM price scenario” (HAMs), in which the price of AM was increased by 100% (to €2.0/kg). This scenario hypothesized the possibility of grant policies that incentivize greener processes, in particular, the production of bio-based AM. Values of MLMP lower than €50/tDRY were considered not realistic (Shen et al., 2019).

The minimum market values for different technical lignins are displayed in Fig. 5 (dotted line): €250/tDRY for soda lignin (SL) and lignosulfonates (LS), €350/tDRY for Kraft lignin (KL), €220/tDRY for hydrolysis lignin (HL), and €500/tDRY for organosolv lignin (OL) (Hodásová et al., 2015). These results were obtained assuming that different lignin feedstocks have different reactivity.

The concept of reactive lignin is linked to the structure and quality of the different technical lignins. The higher price associated with a higher quality of lignin is not enough to guarantee higher conversions, yields, or profitability. The lignin reactivity implies that a given technical lignin is more or less suitable to be converted with high yields not only depending on its characteristics of molecular weight distribution, percentage of functional groups, or chemical linkages but also depending on how those characteristics match with the conversion reactions. Hence, the overall process profitability is expected to vary in function of the specific lignin reactivity in the selected conversion processes. To assess how the lignin reactivities can influence the overall process economics, sensitivity analysis were carried out varying the selling prices of the products according to the three scenarios proposed.

The superstructure, including all the process paths evaluated in this optimization study, with their respective technologies, is plotted in Fig. 4. For each scenario, the optimization provides only one optimal path. For Cs and reactive lignin percentages up to 65%, it will be convenient to follow the path J1 K7, J2 K4 and J3 K4 (in yellow), while for percentages of reactive lignin higher than 65%, the preferable process will be J1 K9, J2 K5 and J3 K4 (in green). As for LAAs, J1 K27, J2 K4, and J3 K4 (in yellow) is also the best solution for low percentages of reactive lignin, whereas for higher percentages of reactive lignin, J1 K6, J2 K2 and J3 K2 (in purple) is preferred. Eventually, when HAMs are considered, J1 K1, J2 K3 and J3 K1 (in orange) is obtained as the optimal process pathway for lower percentages of reactive lignin, whereas for the higher percentages, the preferred upgrading technology will be J2 K1 (rather than J2 K3).

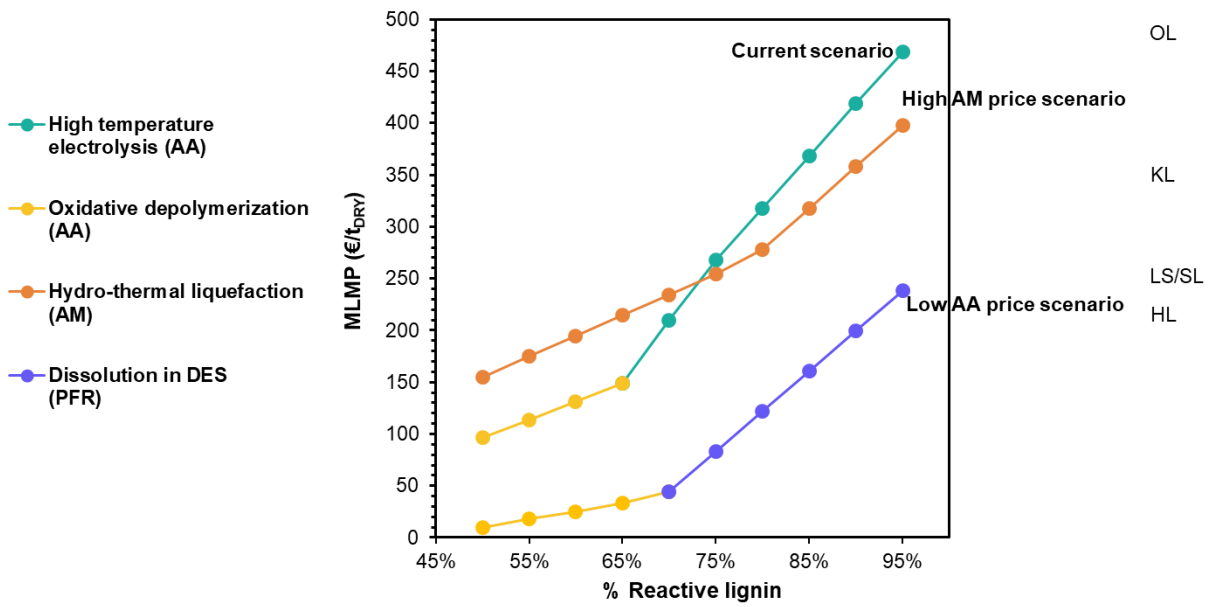


Figure 5. Sensitivity analysis of reactive lignin percentage vs maximum lignin market price varying the selling prices of the products for the three scenarios proposed. (MLMP, maximum lignin market price; OL, organosolv lignin; KL, Kraft lignin; LS, lignosulfonates; SL, soda lignin; HL, hydrolysis lignin)

From an economic perspective, data in Fig. 5 indicated that when the Cs scenario is considered, the oxidative depolymerization (in yellow) resulted in the optimal treatment to convert low reactive lignin, such as LS or HL where the range of reactivity can be considered between 60–80%; while for highly reactive lignin, HTE (in green) is preferable. The elevated capital costs of HTE imply that if the percentage of reactive lignin is not high enough, this process path will not be profitable and, instead, it will be convenient to convert the lignin through oxidative depolymerization, which is a relatively more economical process.

In the LAAs scenario, oxidative depolymerization (in yellow) still resulted in the optimal conversion technology for low reactive lignin. For an elevated percentage of reactive lignin, dissolution in DES (in purple) resulted in the optimal depolymerization treatment. However, this process is still on a laboratory scale and has high capital and operating costs that could be feasible only if high depolymerization yields are reached.

In the third scenario (HAMs), where the selling price of AM was increased up to €2.0/kg, hydrothermal liquefaction (in orange) became the optimal main treatment technology for any lignin reactivity (Fig. 5).

KL, with an assumed reactivity of 70–90% could be considered as a suitable feedstock to reach a profitable MLMP. The slope of the curve representing the costs of HTL indicated that these are similar to those of oxidative depolymerization for a lignin reactivity up to 80% and similar to those of HTE for lignin reactivity above 80%. The convenience of one process pathway over the other is then determined not by the main treatment but by the upgrading technology, i.e., for lower reactive lignin. The catalytic upgrading presents lower costs, while for higher reactive lignin, mild HDO, which is also the more expensive operation, turned out to be the optimum upgrading technology option.

MLMP reported in Fig. 5 shows that a MLMP larger than €150/tDRY is acceptable for AA selling price higher than €15.0/kg, for PFRs selling price higher than €0.8/kg when the percentage of reactive lignin is high, or for AM selling price larger than €2.0/kg. Although yields to AA are low, this is the optimal product when assuming the current market scenario, as its selling price is larger than €15.0/kg. The most feasible production technology for AA production resulted in oxidative depolymerization for lower qualities lignin in terms of specific reactivity (until 65% of reactive lignin) and HTE for higher reactive lignin. For PFRs, dissolution in DES is promising even if it is mainly investigated at laboratory scale. In the case of AM, hydrothermal liquefaction maximizes the economic exploitation of lignin.

An average reactive lignin percentage of 75% was fixed for each scenario to assess and compare the revenues and costs of production of the three target products (AA, AM, or PFR). The operating costs play the main role, as the consumption of utilities (especially medium pressure steam and electricity for the HTE), the consumption of chemicals, solvents (even if solvent recycling was considered) and, particularly, the catalyst that can widely vary depending on each process pathway.

Fig. 6a shows the cost breakdown of the three different scenarios. In these graphs, costs are calculated per unit ton of dry lignin to become independent of the plant size. In the case of AA production, the operating costs (OC) amount to about €479/tDRY, mainly due to the ethyl acetate consumption (€291/tDRY) and electricity consumption (€149/tDRY), with less significant investment costs (IC) (main treatment €10/tDRY, upgrading €8/tDRY, and purification €2/tDRY). From Fig. 6b it can be seen that the yield to AA is only 5%. Nevertheless, revenues for these conditions are €754/tDRY with a profit margin of €275/tDRY, which can be derived from the inspection of the histograms outlined in Fig. 6a as the difference between revenues and costs. This is due to the high selling price of AA in the current market. The challenging limit concerning AA lies mainly in its low yields. This is because specific monomers are needed to obtain the desired group of molecules, making this process highly selective. The aim is, therefore, to find a way to increase the selectivity in the lignin transformation to these products, to increase the yield of the process, making it more cost-effective. To explore how to increase lignin selectivity to AA, catalyzed oxidative depolymerization was further assessed by sensitivity analysis.

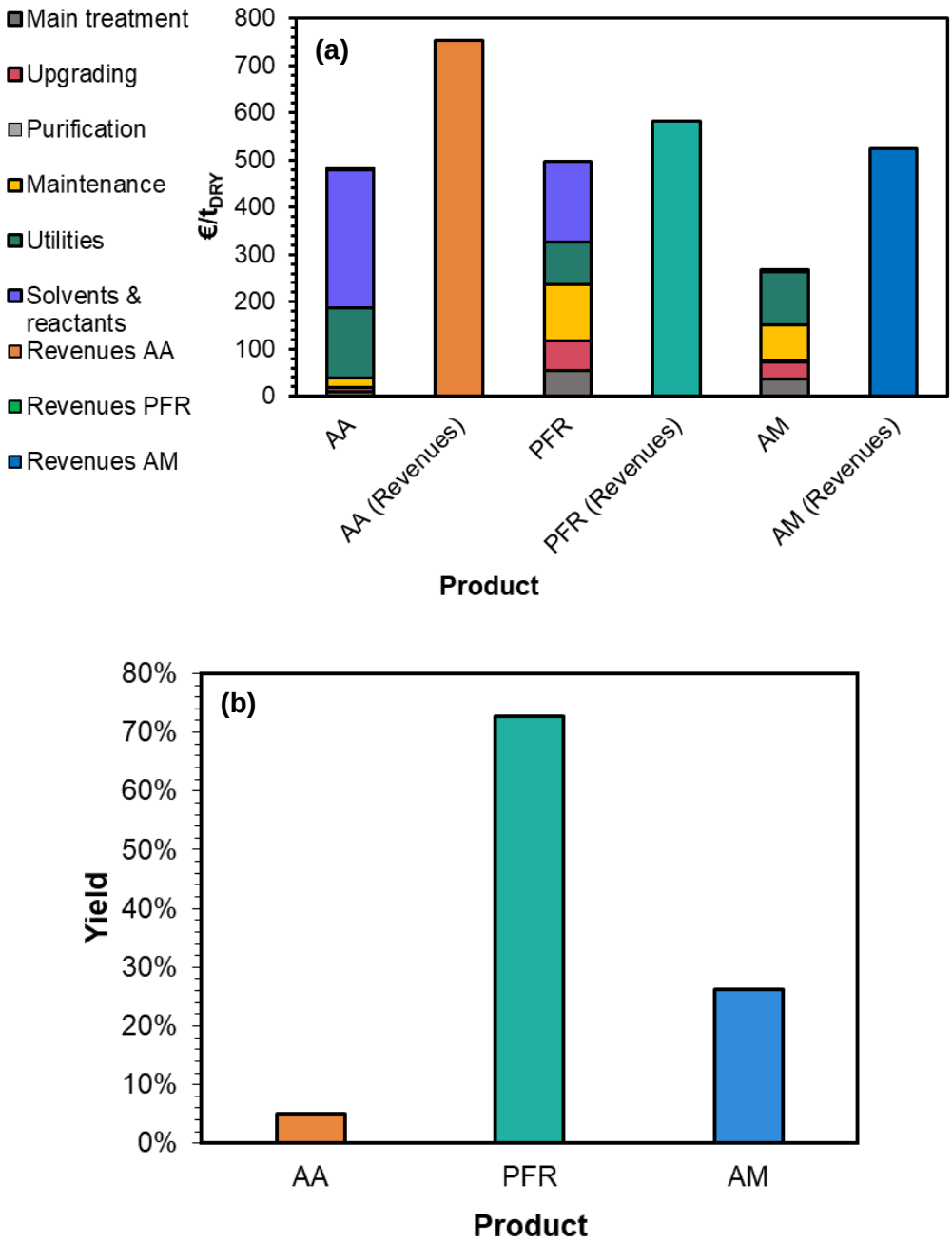


Figure 6. (a) Production cost distribution and product sales revenues; (b) Yields, purity, and recovery rates of vanillin during valorization.

Related to resins production, the OC are slightly higher than the previous case, €496/tDRY. The most significant cost contributions are solvent consumption (€170/tDRY) and maintenance (€118/tDRY) due to the DES make-up cost. In addition, significant IC are significant (main treatment €55/tDRY, upgrading €64/tDRY), again attributed to the expensive main treatment, dissolution in DES, which is still an emerging technology (Fig. 6a). As can be seen in Fig. 6b, the yield to PFR was around 73%. With a selling price of €0.8/kg and revenues of €582/tDRY, the profit margin is only €86/tDRY. Challenges to resins mostly concern their selling price, as they are heavily dependent on the quality of the lignin-derived resin, which is not currently competitive with those derived from petroleum. The profit could also be increased by reducing

costs regarding dissolution in DES, which is a process that is still in its early stage and could have a crucial impact on the product's final quality.

In the case of AM production, the OC grows to €268/tDRY, mainly due to utilities, €118/tDRY. Revenues are high in this optimistic scenario towards AA (€256/tDRY), under a 100% higher product selling price assumption. An unfavorable situation with low yields (26%) and low product selling prices can be observed. The challenge again comes to enhance lignin conversion into products, as well as increase the final product quality.

Producing AA generates a significant return, but the importance of increasing the yield in this process remains of utmost importance. Being this a selective process, increasing the conversion of a certain product requires an improvement of the selectivity. This increment was studied and included as an alternative path in the superstructure as catalyzed oxidative depolymerization. In a V–Cu catalyzed oxidative depolymerization, the total amount of the five aromatic aldehydes and acids increased up to 7.0% (Walch et al., 2021). This corresponds to an increment of 40% for the HTE and 350% for the oxidative depolymerization, assuming 75% of reactive lignin. The highest operational cost in this process is the make-up of the catalyst. If the recovery of the catalyst could be applied up to 95%, without modifying the yield to AA, or a less expensive catalyst would be developed with 10% of the current cost, the profit of this process could be significantly improved, reaching positive values of MLMP from a 55% of reactive lignin. Recycling the catalyst showed lower yields to vanillin than the control experiment (Walch et al., 2021) and due to the high operational costs caused by the high price of the catalyst studied, makes it an economically unviable solution

The valorization of technical lignins to bio-based products has the potential to replace fossil-based aromatics with bio-based chemicals and building blocks. Among bio-based products, AA, AM, and PFR, which are often intermediate in the synthesis of other products, have estimated market sizes of 16 kt/y, 40,000 kt/y, and 1700 kt/y, respectively (Mottaghi et al., 2022). The scientific literature on lignin valorization report findings at different scales, making it difficult to develop a clear framework of the most profitable products from a selected lignin feedstock. The methodology proposed in this paper is aimed to establish the most profitable option to valorize lignin and provides a valuable tool to examine and quantify the gap in the potential market application of lignin. In the present investigation, the superstructure was built including novel and promising processes such as HTE, catalyzed oxidative depolymerization, and DES dissolution whose potentiality at higher TRL can be explored.

To account for the different technical lignins, the concept of reactive lignin was adopted. Kraft lignin has a minimum market price of €260/t, consistent with industrial data (Moretti et al., 2021), which resulted in lower than the MLMP output for both AA and AM assuming a specific reactivity higher than 70% (see Fig. 5). Under these premises, KL resulted an apt raw material to be converted into these chemicals, similarly to LS, and SL. HL has a market value of about €100/t, as estimated by Shen et al. (2019); and resulted suitable for the production of phenols and jet fuels. OL has a market value that goes up to €500/t, as estimated by Mabrouk et al. (2018) in line with its production costs (Moretti et al., 2021). The current analysis found that the application of this type of high-quality lignin is advised only for target products different from AM, AA, or PFR.

Process superstructure optimization indicated that AA through HTE appears to be the most cost-effective lignin-derived product despite its low yields. Promising perspectives were also reported by Wongtanyawat et al. (2018) and Abdelaziz et al. (2020) even in the case of AA price lower than 15.0 €/kg but with process yields higher than 3 %. The novel process based on the use of HTE would enable conversions up to 5% from lignins assuming a reactivity in the range of 60 – 80% (see supplementary material). As an alternative to HTE catalyzed oxidative depolymerization resulted optimal when the transition-metal catalyst can be 90% recycled or if a more economical catalyst with a cost of 10% of the actual would be developed. This emphasized the potential improvement in the catalyst features to achieve more efficient and sustainable processes.

The results in the table/graph indicated that AM could be competitive with respect to AA or PFR only for selling prices of about 2.0 €/kg. This conclusion is in agreement with the techno-economic studies performed by Dessbesell et al. (2018), Ou et al. (2021), and Mabrouk et al. (2017) on the conversion of OS. HTL resulted the most favorable path to AM, this was confirmed by Funkenbusch et al. (2019), that studied an innovative process to produce BTEX mixtures in a continuous catalytic near-critical water reactor for hydrothermal liquefaction because it seems the best process for that. According to Gursel et al. (2019) and Otromke et al. (2019), found that direct HDO presents higher revenues compared to pyrolysis . From the investigation performed in this paper, it was found that HDO is the most promising treatment only if the percentage of reactive lignin is above 80%.

Lignin has a phenolic structure that can be exploited for the production of PFR mainly used as wood adhesives (Shen et al., 2019). PFR resulted in being cost-effective when produced from low-price lignins with a MPLM lower than 100 €/t and a reactive index of 75%. These results are possible due to the outstanding high yields lignin has towards PFR (Fig. 6b), because also with lower lignin reactivity the final yield to the target product (PFR) is sustainable.

Overall, based on the superstructure developed in the present paper AM, AA, or PFR obtained from mid and lower quality lignins, such as HL, LS, and SL, associated with lower yields can still be profitable.

In the present paper mass balance was estimated using the concept of reactive lignin to be independent of the quality and characteristics of the lignin used as feedstock. The product yields are importantly dependent on the lignin characteristics Therefore, the way to relate the specific lignin reactivity to measurable lignin characteristics is a subject for further research. For instance, in reactions involving a depolymerization process, the molecular weight distribution could as the first approximation be used as an index associated with specific reactivity and provide a numerical difference between different lignins.

3. Techno-economic analysis and life cycle assessment of lignin (catalytic) fast pyrolysis towards phenolics and aromatics (HVAC)

Techno-economic analyses and life cycle assessments were performed for 8 scenarios of lignin non-catalytic and catalytic fast pyrolysis towards the production of high value-added chemicals (phenolics and BTX aromatics) (Iakovou et al., 2023; Iakovou, 2021). Electric energy production was studied as base case, while the rest scenarios resulted in bio-oil separation and recovery of single compounds or fractions (groups of compounds). Three different technologies have been studied: a) simulated moving bed chromatography (SMB) which provides the means for acquiring distinct high purity compounds from the bio-oil, b) Distillation, and c) liquid-liquid extraction leads to bio-oil fractions of chemical groups. Table 4 presents the different scenarios under study.

The goal of this study was to compare scenarios of production of high value-added chemicals from lignin fast pyrolysis with 3 variant parameters: Type of feedstock, process type (thermal or catalytic pyrolysis) and chemicals separation method. Kraft lignin is a product of treating black liquor, thus a significant amount of processing is required in order to recover it. When purchased by the "pyrolysis industry" as feedstock, the cost is slightly lower than that of organosolv lignin. However, if it is produced and used by an on-site pyrolysis unit, for example in a paper mill, then the cost of Kraft lignin as feedstock is much lower and a significant betterment of the economic results is to be expected. In order to maintain consistency in the comparison, both Kraft and organosolv lignins were considered to be purchased from outside sources.

The study found that while Kraft lignin is slightly cheaper, organosolv performs better when using a catalyst.

Regarding the process, economic performance of thermal pyrolysis seems to be a better option in combination with the use of simulated moving bed chromatography while catalytic pyrolysis can give higher value-added chemicals and it all depends on the type of the needed products (Figure 7).

The separation technique is directly linked to the Investment cost as well as the production cost and it should be selected on the grounds of the required chemicals. The processes should be tested on a pilot scale before considering scaling them up since the investment costs reach in some cases the number of 377 million euros.

Separation techniques are of high interest as far as separation of the bio-oil goes and a lot of research work is to be expected to be done.

One of the most important aspect of the potential application of lignin fast pyrolysis as a process for acquiring high value-added chemicals is studying market needs and trends. The process may be able to produce 60 kg/h of a specific component which may have a present market value of thousands of euros, however, this doesn't mean that the market can absorb said chemical in such quantities. Market over-saturation may bring a significant price drop which could potentially break the specific investment plan and a lot of work is expected to be done in this field.

Table 4. Scenarios of lignin fast pyrolysis towards the production of high value-added chemicals

Scenario	Lignin	Process type	Main Product
1	Kraft	Fast Pyrolysis, Thermal	Electric energy production
2	Kraft	Fast Pyrolysis, Catalytic	Electric energy production
3	Organosolv	Fast Pyrolysis, Thermal	Electric energy production
4	Organosolv	Fast Pyrolysis, Catalytic	Electric energy production
5	Kraft	Fast Pyrolysis, Thermal	HVACs (SMB)
6	Kraft	Fast Pyrolysis, Thermal	HVACs (Distillation)
7	Kraft	Fast Pyrolysis, Thermal	HVACs (Liquid-liquid extraction)
8	Kraft	Fast Pyrolysis, Catalytic	HVACs (SMB)

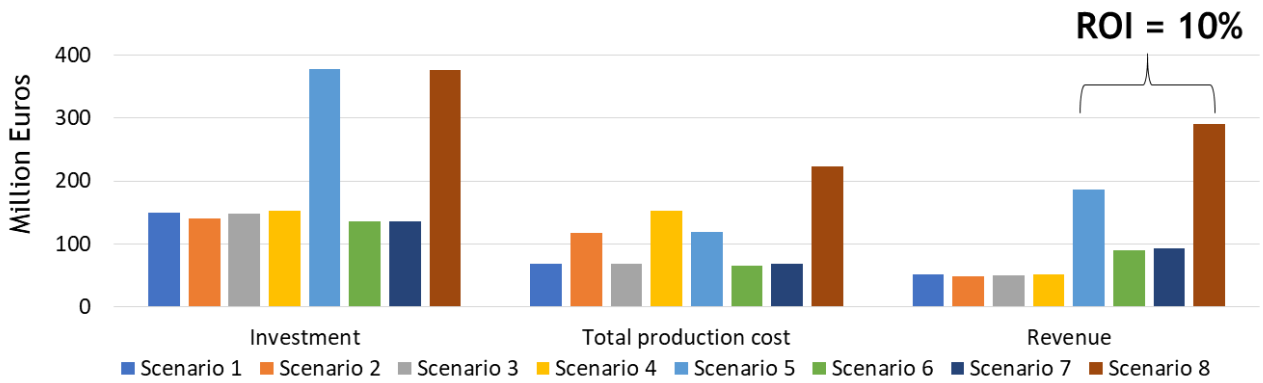


Figure 7. Techno-economic analyses for each scenario regarding investment, total production cost and revenue.

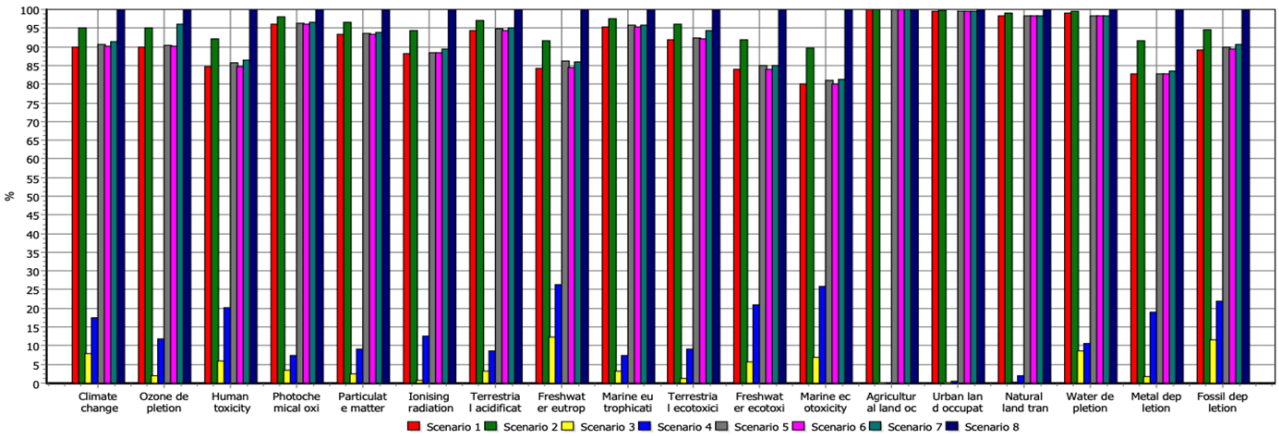


Figure 8. Environmental analyses for each scenario (FU: 1kg of HVACs).

Investment and production cost are higher for catalytic fast pyrolysis using SMB for separating the bio-oil to single compounds, but the revenues are also substantially higher. The selling prices of HVACs in Scenarios 5 to 8 were designed with a Return on Investment of 10% as a goal.

Regarding the environmental impact (Figure 8), catalytic fast pyrolysis has a slightly more pronounced effect on all impact categories compared to thermal pyrolysis. Distillation and liquid-liquid extraction as separation methods have similar environmental performance. Although SMB (with single HVACs as the main products) induces slightly more pronounced effect, the differences between all three separation methods are no more than 15%.

4. Techno-economic and environmental sustainability assessment of Kraft lignin valorization for bio-adhesives production

This study focusses on the techno-economic assessment (TEA) and Life Cycle Assessment (LCA) of Kraft lignin conversion into bio-oil and oligomers via base-catalyzed depolymerization for the production of bio-adhesives for wood-based panel applications. Market price fluctuation and operating costs have been considered as variables to assess their effect on the techno-economic performance of this process.

4.1 Process description and design

An extended literature review was performed during the LignoCOST Action evaluating the suitability of different types of lignin (e.g. Kraft, soda, organosolv, alkali and lignosulfonates among others) for the production of bio-based adhesives by replacing the phenolic content of conventional PF resins (Abdelwahab et al., 2011; Cheng et al., 2013; Ghorbani et al., 2016; Gosselink et al., 2010; Kalami et al., 2017; Lee et al., 2011; Luo et al., 2020; Papadopoulou et al., 2018; Solt et al., 2019; Solt et al., 2018; Tachon et al., 2016). The process presented by Solt et al. (2018) has been employed for lignin processing via base-catalyzed depolymerization (BCD) to obtain the two lignin fractions, namely BCD-oil and BCD-oligomers bio-based phenolic compounds. This case was selected as it depicts the best initial lignin characteristics (molecular weight and polydispersity index) for further valorization, the experimental results have been developed in pilot scale bioreactor and the produced bio-based phenolic compounds can substitute up to 70% of conventional phenolic content in reference resins (Solt et al., 2018).

Mass and energy balances, process flow compositions and equipment sizing were carried out using the process design software Unisim (Honeywell) considering 10,000-100,000 t/year annual production capacities of total products (BCD-oligomers and BCD-oil). The lignin depolymerization process operates 7920 h/year.

The process (Figure 9) starts with the dissolution of lignin in a sodium hydroxide solution in a mixing tank (V-101). The mixture is then fed into the continuous high-pressure reactor (FR-101) operating at 250 bar with a high-pressure pump (HP-101), 320°C and a residence time of 10 minutes. Under these conditions, hydrolysis takes place to obtain low molecular weight oligomers, due to the cleavage of the aryl-aryl and aryl-methyl-ether bonds present in lignin. After completion of the reaction, the temperature of the stream decreases by energy exchange with the inlet stream (E-101) and the pressure is reduced to ambient levels prior to the downstream separation and purification (DSP) stage. Some volatile organic compounds (methanol, formic and acetic acid) are produced during the reaction, which are collected and sent to the combined heat and power (CHP) unit, which supplies electricity and steam to the plant, reducing its energy needs (Humbird et al., 2011).

The DSP stage begins with the precipitation of the BCD-oligomers under acidic conditions using HCl. The BCD-oligomers are subsequently separated with a chamber filter press (F-101). After separation of the BCD-oligomers, the bio-oil permeate-rich solution is concentrated five times using a mechanical vapor recompression (MVR) evaporator (EV-101). The condensed water from the evaporation process is recirculated and the concentrated stream is fed to the liquid-liquid extraction unit (LLEXV-101) where the bio-oil is separated from the aqueous solution using methyl isobutyl ketone (MIBK). After liquid-liquid extraction, decanting (DV-101) is carried out to separate the organics from the aqueous phase. In this step, sodium sulphate salts are used to reduce the miscibility of MIBK in water. This is followed by the bio-oil recovery step by evaporation of the MIBK in the MVR evaporator (EV-102) and recirculation to the liquid-liquid extraction unit. The salts are dried using a spray dryer (DR-102) and reused in the decanting step

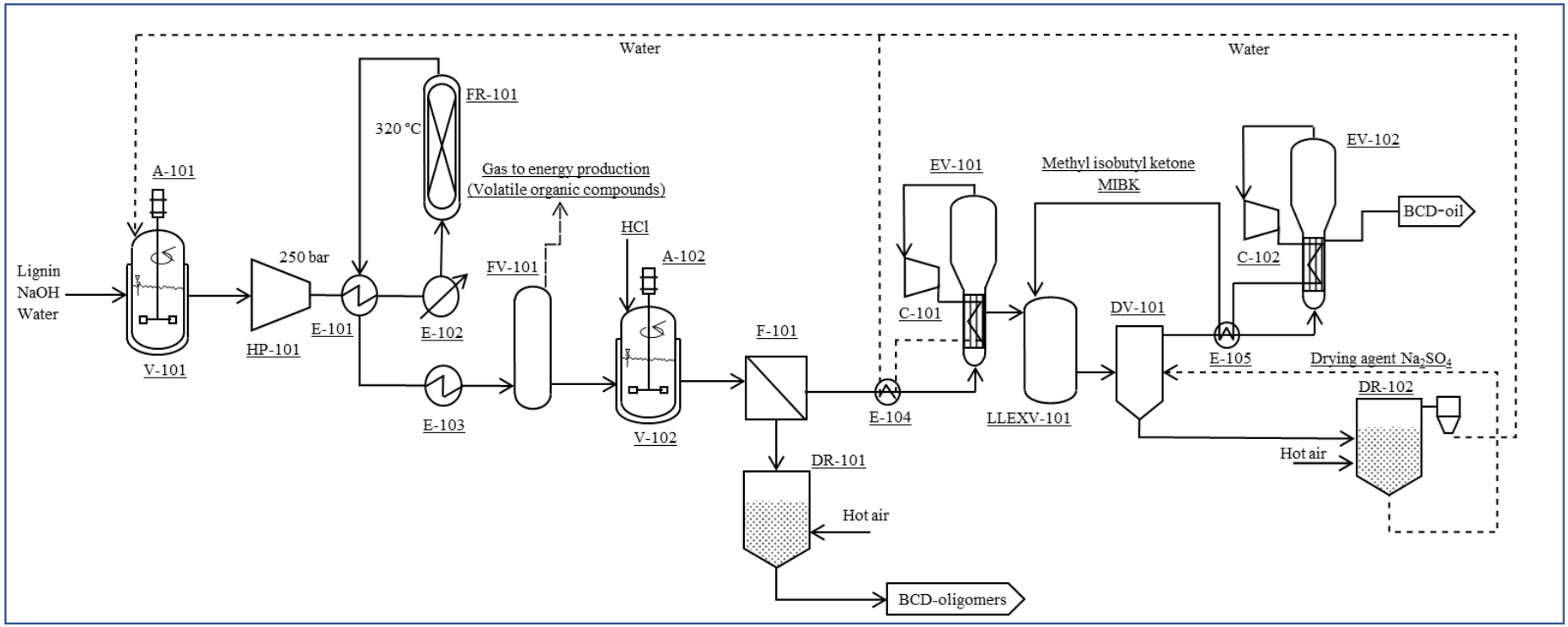


Figure 9. Process flow diagram of lignin conversion into BCD-oligomers and BCD-oil. Abbreviations: HP (High Pressure Pump), E (Heat Exchanger), FR (Flow Reactor), DV (Decanter), F (Filter), DR (Dryer), V (Vessel), A (Agitator), FV (Flash Vessel), LLEXV (Liquid-Liquid Exchange Vessel)

4.2 Life cycle assessment

In order to assess the environmental burdens associated with the valorization of lignin for the production of BCD-oil and BCD-oligomers, the LCA methodology has been applied. The base case scenario has been based on considering the functional unit (FU) of the valorization process of 1 kg of Kraft lignin. The reason for the selection of a mass-based FU is based on the easier comparison with other non-renewable resources, such as fossil fuels. In terms of system boundaries, a "cradle to gate" approach has been considered in order to identify the environmental burdens of the lignin recovery process, from the production of Kraft lignin (cradle) to the production of bio-oil and oligomers for the production of bio-adhesives (gate). The performed LCA has been based on the use of the EcoInvent database, within the European context. As the database for Kraft lignin is not available in the EcoInvent database, literature data has been used to assess the environmental loads associated and their allocation in the context of the overall process (Bernier et al., 2013). Regarding the methodology used to determine the environmental impacts, the recommendations of the Environmental Footprint/ILCD (Finkbeiner, 2011) have been considered. For this purpose, the impact categories assessed, together with the method used for their calculation, are shown in Table 5. Furthermore, to computationally implement the inventory data, the software SimaPro (PRé Consultants, 2004) has been used and the ReCiPe EndPoint methodology was used to evaluate the comparison between the bioadhesive scenarios, together with the phenol formaldehyde fossil-based adhesive scenario.

4.3 Results – Techno-economic performance

Figure 10A presents the FCI of the whole process presented in Figure 9 considering different plant capacities to produce both products (BCD-oligomers and BCD-oil). The FCI is decreased with increasing plant capacities due to the economies of scale up to a constant value. The highest FCI ($2.44/kg) was estimated at the lowest production capacity (10,000 t/year). Limited changes in the FCI values are observed from a threshold annual production capacity of 50,000 t/year. The lowest FCI ($1.03/kg) was estimated at 100,000 t/year production capacity. The annual production capacity of 50,000 t/year was considered as the optimal plant capacity (OPC) for this process. Table 6 presents the costs of FOB purchase equipment (Ceq.fob), FCI, workers, COL, utility requirements and CUT at the OPC.

Table 5. Recommended methodologies for calculating impact categories values. Adapted from the Environmental Footprint recommendations Annexes 1-2.

Category	Indicator	Methodology
CC	Global warming potential, kg CO2 eq.	IPCC 2013 model
OD	Ozone depletion potential, kg CFC11 eq	EDIP model
HT,c	Comparative toxic unit for humans, CTUb	USEtox 2.1 model
AD	Accumulated exceedance (AE), mol H+ eq	ILCD
ET	Accumulated exceedance (AE), mol N eq	ILCD
EF	Fraction of nutrients reaching freshwater, kg P eq	ReCiPe 2016
EM	Fraction of nutrients reaching marine, kg N eq	ReCiPe 2016
TF	Comparative toxic unit for ecosystems, CTUe	USEtox 2.1 model
RM	Abiotic resource depletion, kg Sb eq	CML 2002
RF	Abiotic resource depletion-fossil fuels, kg oil eq	ReCiPe 2016

Table 6. FOB purchase equipment cost ($C_{eq.fob}$), FCI, workers, C_{OL}, utility requirements and C_{UT} for 50,000 t/year total products (BCD-oligomers and BCD-oil) production capacity.

Unit operation	Description	$CEPCI_{t0}$ [d]	Characteristic size (X_t) [e]	FOB Cost ($C_{eq.fob}$ @ 2020, M$)	Electricity (MWh/y)	Steam (t/y)	Natural gas (kg/y)
V-101	Mixing tank[a]	521.9	V=75 m^3	0.200			
A-101	Agitator[a]	521.9	P=64 hp	0.119	382.35		
HP-101	High pressure Compressor[c]	390.6	P=890 kW	0.384	7,052.28		
E-101	Heat exchange[a]	521.9	A= 236 m^2	0.103			
E-102	Heater (4 units) [c]	397.0	Duty=8,128.67 kW	1.276			4,864.20
FR-101	Flow reactor[c]	397.0	V=20 m^3	0.094			
E-103	Heat exchanger-Air cooler (2 units)[c]	397.0	A=78.6 m^2	0.138			
FV-101	Flash Tank[a]	521.9	V=75 m^3	0.200			
V-102	Mixing tank[a]	521.9	V=75 m^3	0.200			
A-102	Agitator[a]	521.9	P=64 hp	0.119	382.35		
F-101	Filter[b]	344.0	A=242 m^2	0.335	94.40		
DR-101	Dryer[c]	390.6	Q=1.13 kg/s	0.567	107.56		
EV-101	Evaporator[a]	521.9	A= 404 m^2	3.807			
C-101	Compressor[a]	521.9	P=2,331 kW	0.508	17,783.25		
E-104	Heat exchanger (2 units)[a]	444.2	A= 553 m^2	0.431			
LLEXV-101	Liquid-Liquid Exchange Vessel[a]	521.9	V=150 m^3	0.304	764.71		
DV-101	Decanting Tank[c]	397.0	V=36 m^3	0.078			
EV-102	Evaporator[a]	521.9	A= 11 m^2	0.435			
C-102	Compressor[a]	521.9	P=8 kW	0.032	56.04		
E-105	Heat exchanger[a]	444.2	A=33.63 m^2	0.034			
DR-102	Dryer[d]	390.6	Q=0.28 kg/s	0.430	26.89		
CHP	Turbogenerator			2.737	Produced 14,088.55	Produced 28.86	Consumed 330,961
Unitary utility cost					0.0674 $/kWh	$9.45 /t	$0.165 /kg
Workers			**6**				
Total Ceq.fob (M$)				**12.517**			
FCI (M$)			**5 × Total $C_{eq.fob}$ =**	**62.585**	**C_{UT} (M$/y) =**		**0.89**

FOB purchase equipment cost (Cp) estimation: [a] Dheskali et al., 2017; [b] Peters et al. 2003; Turton et al., 2018; [d] $CEPCI_{t0}$: Chemical Engineering Plant Cost Index at the year where the purchase equipment cost (C_{p,t_0}) is available considering a characteristic size (X_{t_0}); [e] Xt: is the characteristic size of each unit operation estimated in this study via process design and used for the estimation of the FOB purchase equipment cost at 2020 as follows $C_{p,2020} = \frac{CEPCI_{2018}}{CEPCI_{t_0}} C_{p,t_0} \left(\frac{X_t}{X_{t_0}}\right)^n$

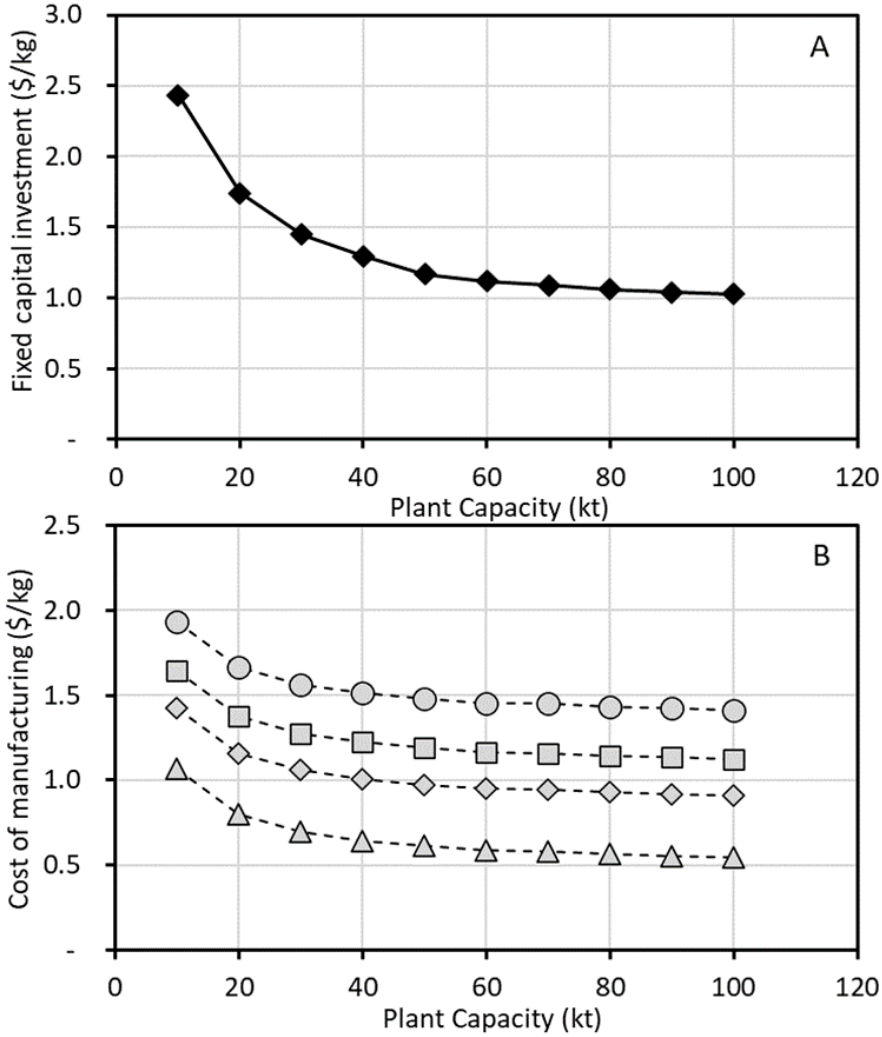


Figure 10. FCI (A) and COM (B) expressed per kg total products (BCD-oligomers and BCD-oil) estimated at different plant production capacities (10,000–100,000 t/year). The COM was estimated taking into consideration different market prices for Kraft lignin (△) $100/t, (◊) $350/t, (▢) $500/t, (●) $700/t.

The COM (Figure 10B) was estimated taking into consideration the different purchase market prices of Kraft lignin ($100-700/t) as the dominant raw material for this process. Different lignin market prices were considered to assess the influence of market price fluctuation on the COM of lignin depolymerization. The COM for each lignin market price was estimated at different plant capacities (10,000-100,000 t/year) (Figure 10B). At the OPC (50,000 t/year), the COM ranged from $0.61/kg to $1.48/kg when Kraft lignin market prices varied from $100/t to $700/t. The purchase market price of lignin has a significant influence on the COM of lignin depolymerization.

Two different MSP values were estimated for BCD-oligomers and BCD-oil fractions of bio-based phenolic compounds. The estimation of each MSP value was based on the estimation of separate FCI and COM values for each product (BCD-oligomers and BCD-oil). More specifically, in the process flow diagram of Figure 9 the unit operations from the mixing tank (V-101) to the first evaporator (EV-101) and the dryer (DR-101) are common for the production of both BCD-oligomers and BCD-oil. When the OPC is considered (50,000 t/year), the process presented in Figure 9 leads to the production of 36,400 t/year BCD-oligomers (72.7% of the total production) and 13,600 t/year BCD-oil (27.3% of the total production). After the estimation of the FCI and

COM for the unit operations starting at the mixing tank (V-101) to the first evaporator (EV-101) (Figure 9), the respective FCI and COM of BCD-oligomers production for this specific section and the FCI and COM of BCD-oil production for this specific section have been estimated using the mass ratio of BCD-oligomers (72.7%) and BCD-oil (27.3%) production. Thus, the FCI and COM of BCD-oligomers production is the 72.7% of the FCI and COM of the unit operations starting at the mixing tank (V-101) to the first evaporator (EV-101) and the dryer (DR-101). The FCI and COM of BCD-oil is the 27.3% of the FCI and COM of the unit operations starting at the mixing tank (V-101) to the first evaporator (EV-101) plus the FCI and COM for the rest of the process using all unit operations presented in the process flow diagram of Figure 1, except for DR-101 that is used only for the production of BCD-oligomers.

The MSP values at the OPC were estimated at $0.65-1.52/kg for the BCD-oligomers (Figure 11A) and $0.78-1.94/kg for the bio-oil (Figure 11B) when the price of Kraft lignin varied in the range $100-700/t. The NPV (Figure 12) was estimated considering different selling prices of the products ($0.8-1.2/kg) and different capacities (10,000-100,000 t/year) at a Kraft lignin market price of $100/kg. The market prices of the products were taken considering the fluctuation of fossil-derived phenol market price ($0.8-1.2/kg) that is used in the manufacture of PF resins (Alibaba.com). The NPV is positive for all product market prices. In particular, at the lowest market price ($0.8/kg) for both products, the NPV is estimated at M$6.5, while a DPP value of 24 years has been estimated. This DPP is not acceptable for industrial plant investments (Zuberi et al., 2017), but it can be reduced to 11 years at 100,000 t/year production capacity. At higher market prices, namely $1.0/kg and $1.2/kg for both products, the DPP was estimated at 8 and 6.5 years, respectively.

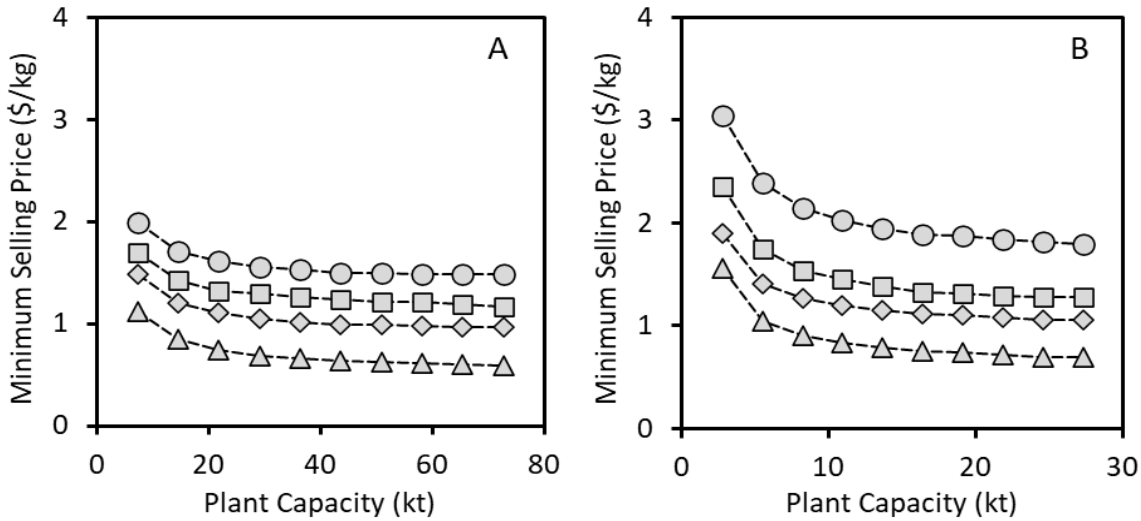


Figure 11. The MSP expressed per kg BCD-oligomers (A) or BCD-oil (B) estimated at different production capacities (A 7.27–72.7 kt/year, B 2.73-27.3 kt/year). The MSP was estimated taking into consideration different market prices for Kraft lignin (△) $100/t, (◊) $350/t, (□) $500/t, (○) $700/t.

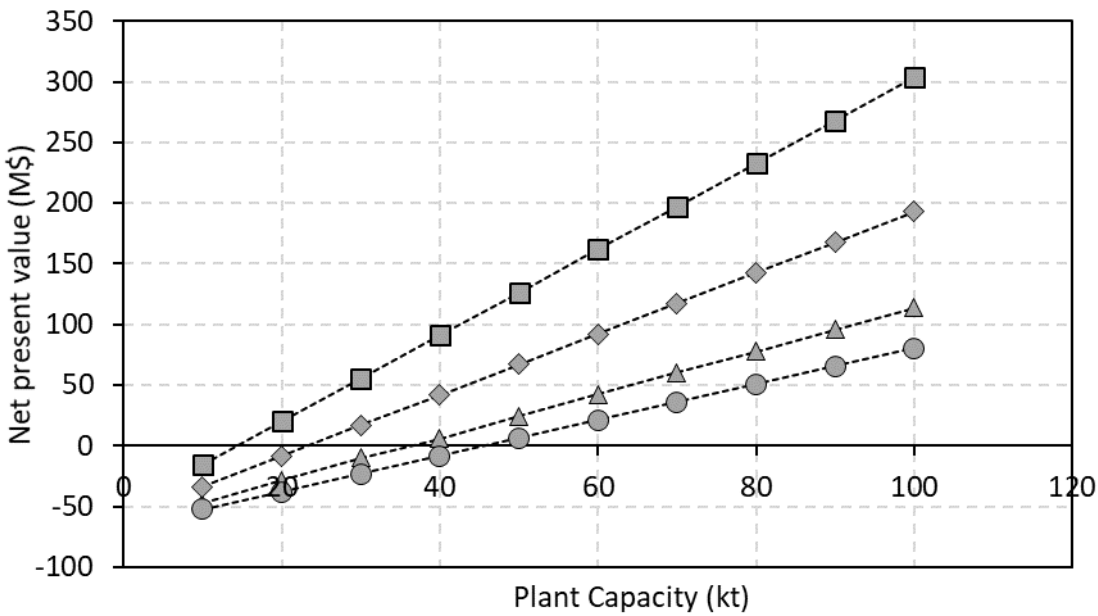


Figure 12. NPV at varying plant production capacities using different selling prices of the BCD-oligomers and BCD-oils. (●) BCD-oligomers $0.8/kg and BCD-oil $0.8/kg, (△) BCD-oligomers $0.8/kg and BCD-oil $1.0/kg, (◇) BCD-oligomers $1.0/kg and BCD-oil $1.0/kg, (▢) BCD-oligomers $1.2/kg and BCD-oil $1.2/kg.

4.3 Results – Environmental performance

The LCA inventory was based on mass and energy balances derived from the process design. The inventory was expressed per kg of Kraft lignin. The overall inventory data used to develop the LCA are shown in Table 7.

Considering the methodologies for the calculation of environmental loads associated with the use of lignin as a renewable raw material for the production of BCD-oligomers and BCD-oil , the following environmental profile has been obtained. Figure 13 shows that the use of chemicals for dissolving lignin (NaOH) and for the precipitation of lignin oligomers (HCl) contribute the highest environmental impact. In particular, NaOH contributes the highest impact, accounting for more than 40% of the overall impact for most of the impact categories assessed. Energy requirements (both natural gas and electricity) are not an issue here, as the largest impact, as expected, is observed in the RF impact category, but it is not the main hotspot that could be identified. On the other hand, it should be noted that the use of Kraft lignin also leads to some impact on the categories, especially in the case of the HT,c category, contributing more than 20% of the overall impact. The reason for this impact is that lignin has not been considered as a zero-impact resource, as it comes from a background process. An appropriate allocation has been made to assign the impact to the black liquor containing this Kraft lignin, in order to take into account, the environmental loads coming from this stream. But in fact, in the sensitivity analysis, this Kraft lignin will also be considered as a zero-impact flow. As this stream is prevented from reaching the environment without being recovered, significant impacts are avoided, so it could be a good approach to consider this Kraft lignin as an "avoided" harmful stream, and this benefit is translated by considering it as a zero-impact input feedstock.

Table 7. Life Cycle Inventory of Kraft lignin conversion into BCD-oligomers and BCD-oil. Functional unit: 1 kg Kraft lignin.

Inputs from technosphere			Outputs to technosphere		
Item	Amount	Unit	Item	Amount	Unit
Kraft lignin	1.00	kg	BCD-oligomers	0.62	kg
NaOH	0.28	kg	BCD-oil	0.23	kg
HCl	0.25	kg			
Energy			Waste to treatment$_{(CHP)}$		
Natural gas	0.08	kg	Condensate gaseous by-products	0.15	kg
Electricity	0.25	kWh			

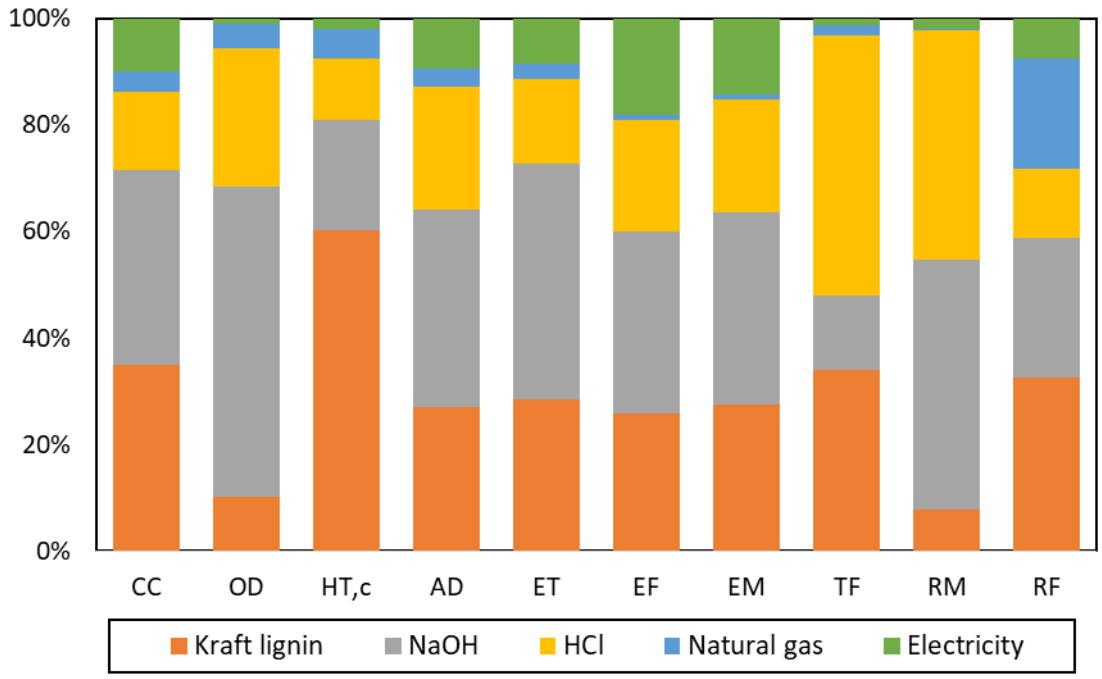


Figure 13. Environmental profile for the production of BCD-oligomers and BCD-oil using lignin as renewable input resource.

Regarding the scoring of the impact category values, Table 8 shows the environmental loads associated with the functional unit. The harmful human toxicity of the lignin processing facility is not great, in fact, it entails negligible health damage. The OD, EM and RM categories have a very low value, reaching only 0.32 mg CFC11 eq, 41.9 mg N eq and 13.4 mg Sb eq per kg of Kraft lignin treated, respectively. This could be considered as a good and sustainable result, as the impact on the ozone layer, eutrophication and mineral resources categories is not significant. The same conclusion has been reached when assessing the AD and ET categories.

Table 8. Impact values associated with lignin valorization for the production of BCD-oligomers and BCD-oil. Functional unit: 1 kg Kraft lignin

Impact category	Value	Unit	Impact category	Value	Unit
CC	0.83	kg CO_2 eq	EF	0.46	g P eq
OD	$3.22 \cdot 10^{-7}$	kg CFC11 eq	EM	0.04	g N eq
HT,c	$7.77 \cdot 10^{-11}$	CTU_b	TF	$2.79 \cdot 10^{-3}$	CTUe
AD	4.81	mmol H^+ eq	RM	13.4	mg Sb eq
ET	8.09	mmol N eq	RF	0.29	kg oil eq

Although the values for the EF and RF categories are slightly higher, they can also be considered as acceptable scores. However, attention has to be paid to the RF value, which amounts to 0.29 kg oil eq/kg Kraft lignin used, which is derived from the energy consumption required to produce the different chemicals used in the background process. To reduce this value, different alternatives can be developed, the first of which would be to increase the productivity of the process by improving the efficiency of the lignin treatment technology, thus making a more efficient use of resources. The second option could focus on the use of renewable energy sources to reduce the consumption of fossil resources. This alternative, although entirely feasible, and possibly the most appropriate from the point of view of environmental sustainability, is outside the system boundaries as it depends on upstream processes of raw materials and chemicals. For this reason, the sensitivity analysis will opt for the use of renewable energies to obtain the necessary energy in the process itself, but given their low contribution to this impact category, the improvement in the value of this impact category would not be significant.

One of the most common applications of lignin derivatives is their use in the formulation of adhesives. In this case, the partial substitution of the phenol content in PF resins by BCD-oligomers and BCD-oil has been proposed and tested. Specifically, according to Solt et al. (2018) the BCD-oligomers could replace 70% of the phenol amount required in PF resins, while in the case of BCD-oil 50% of the phenol could be replaced to keep the tensile strength score at the same value as PF resins.

To this end, three scenarios are proposed to assess the environmental burdens and techno-economic scores, seeking to determine the benefits and suitability of using lignin-oil oligomers for the production of bio-based adhesives. The environmental assessment has been carried out using the ReCiPe EndPoint methodology, as it provides three damage categories and a single score value that encompasses the previously assessed mid-point impact categories. However, the functional unit considered for the study has been modified. In this case, the production of 1 kg of adhesive has been selected, as it is the most widespread when trying to assess and compare the environmental loads of scenarios that have the same purpose, in this case, the production of an adhesive. Furthermore, the environmental data for PF synthetic resin, available in the literature and in the EcoInvent database (Wernet et al., 2016), are based on the same approach: the production of 1 kg of adhesive as a functional unit. The damage loads obtained by applying the ReCiPe EndPoint methodology are represented in Table 5.

Table 9 shows that in all damage categories the substitution of the amount of phenol leads to a reduction of the environmental impact. However, it should be taken into consideration that the production of BCD-oligomers and BCD-oil, even though it is produced from renewable resources, requires the use of chemicals, which entails a certain environmental contribution. The fact that non-fossil resources are used as industrial feedstocks does not always mean that the impacts on the environment are less, as the process of their valorization requires the use of chemicals and energy of fossil origin. On the other hand, the damage score

of the proposed alternative scenarios could be considered as a more sustainable option when partial substitution of PF resins is sought. But the fact that the amount of formaldehyde is the same, which has the highest impact in the human health damage category, due to its toxicity and carcinogenic potential, results in a lower improved score in the human toxicity damage category, with a damage reduction of 22% and 15% for the BCD-oligomers and BCD-oil bio-adhesives, respectively (Figure 14). In the ecosystem and resource damage categories, the use of PF-BCD-oligomer contributes a higher damage reduction compared to PF-BCD-oil bio-adhesive, with a reduced impact value of 53% and 30%, respectively. In this sense, although the variations are not so significant between the two proposed scenarios, it could be established that the PF-BCD-oligomer adhesive alternative is better, from an environmental point of view, as the impact loads are lower.

Table 9. Recipe EndPoint damage loads and single score value of the adhesives scenarios

Damage category	Unit	PF	PF-BCD-oligomers	PF-BCD-oil
Human health	mPt	84.94	66.59	71.88
Ecosystems	mPt	4.03	2.83	3.18
Resources	mPt	7.20	3.38	4.47
Single score	mPt	96.18	72.81	79.53

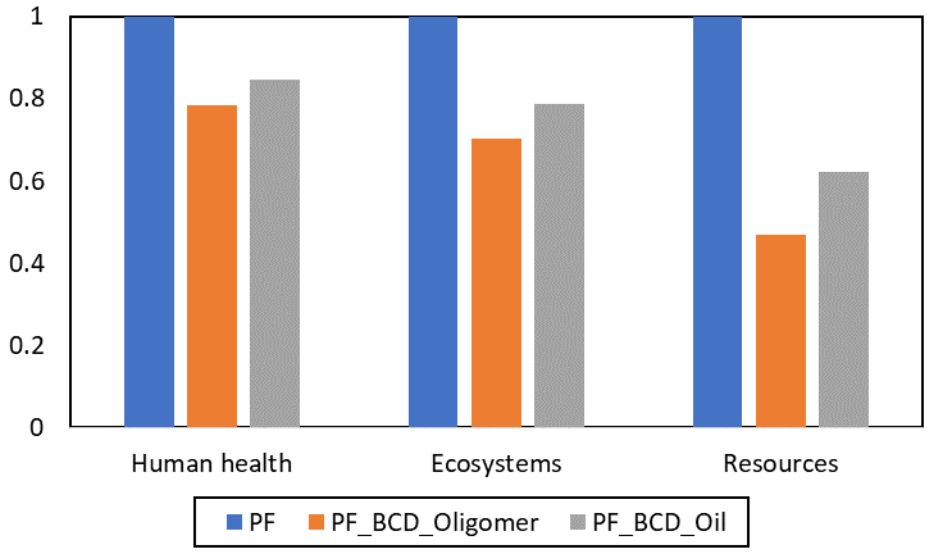


Figure 14. Comparison of the damage loads associated with the alternative adhesives scenarios. Abbreviations: PF (Phenol-formaldehyde), PF-BCD-Oligomers (substitution of phenol in PF resin by 70% with lignin BCD-Oligomers) and PF-BCD-Oil (substitution of phenol in PF resin by 50% with lignin BCD-Oil).

In summary, the valorization of Kraft lignin to produce BCD-oil and BCD-oligomers was found to be a sustainable alternative at the end of its useful life. The LCA methodology and the TEA analysis have confirmed the suitability of the process, when considering a capacity of at least 40,000 t for the facility. To improve the results obtained in this study, future research efforts should focus on reducing the dosage of chemicals, in particular NaOH, due to its contribution on the environmental impact of the production process: the less chemicals, the more sustainability. Although both BCD-oligomers and BCD-oil could be considered as suitable materials to obtain a resin with appropriate mechanical and physical properties, the use of BCD-oligomers seems to be a better option. The justification for this statement is based on the higher percentage of phenol substitution achieved by BCD oligomers, 70%, compared to that of BCD oil, 50%, which results in a lower environmental burden.

Based on the TEA and LCA results obtained in this study, the BCD-oligomers and BCD-oil produced from Kraft lignin could be considered as phenol substitutes for the sustainable production of bio-based adhesive resins for wood-based panel applications. They could contribute to reducing the environmental impacts associated with the production of synthetic PF-based adhesives.

5. Techno-economic and environmental sustainability assessment of Kraft lignin valorization for epoxy resins production

This study focusses on sustainability assessment of epoxy resin production via lignocellulosic biomass utilization through biorefinery concept market price fluctuation and operating costs have been considered as variables to assess their effect on the techno-economic performance of this process.

5.1 Process description and design

The process presented by Asada et al. (2015) has been employed for simulation of the process for bio-based epoxy resins. The whole process divided in 5 Areas:

- Area 100 Pretreatment
- Area 200 Hydrolysis
- Area 300 Succinic acid
- Area 400 Epoxy resins
- Area 500 Energy production

Mass and energy balances, process flow compositions and equipment sizing were estimated using the process design software Unisim (Honeywell) considering 10,000-100,000 t/year annual production capacities for both succinic acid and epoxy resins. The lignin depolymerization process operates 7920 h/year.

The process (Figure 15) starts with the pretreatment (Area 100) of eucalyptus wood biomass by steam explosion process with the high-pressure reactor (HPR-101). The treated biomass is mixed with water (V-101) and the water soluble material is removed by filtration (F-101). The remaining solids stream is dried (DR-101) and then mixed with methanol (V-102). The mixture separated via filtration (F-102) into two streams, one stream is a liquid containing methanol-soluble lignin (a low molecular weight lignin) and the other is a solid stream containing holocellulose and Klason lignin (a high molecular weight lignin), and acid-soluble lignin. From the liquid stream, the methanol is recovered and recirculated by evaporation (EV-101). After evaporation, the methanol-soluble lignin is utilized in AREA 400 for epoxy resin production.

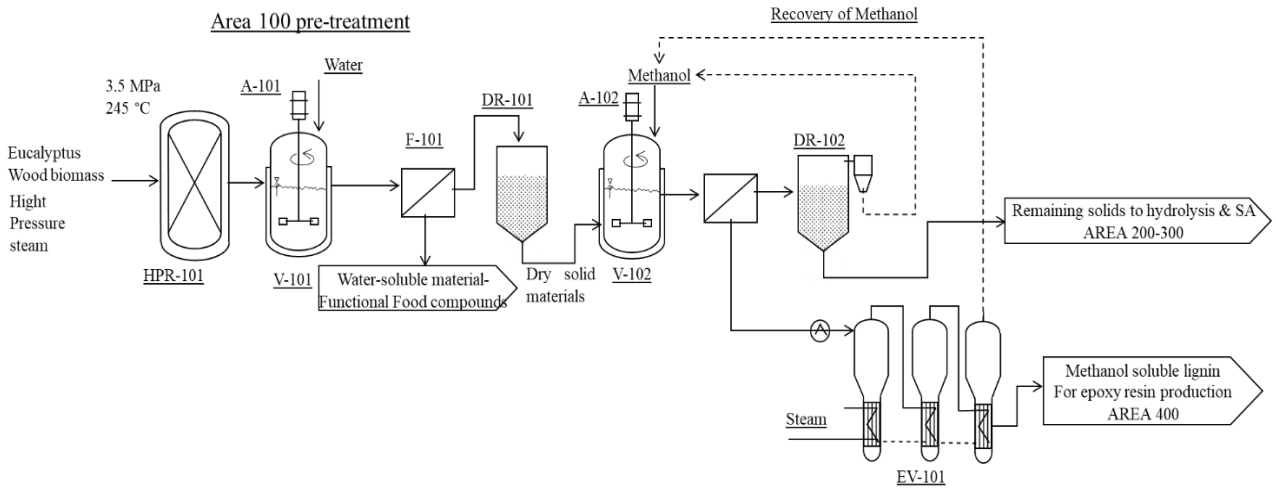
The stream with holocellulose and remaining lignin is used in Area 200 where enzymatic hydrolysis (V-201) takes place. The produced sugars-rich hydrolysate is separated from the remaining solids (Klason and acid soluble lignin) by centrifugation (CF-201). After separation, the stream with remaining solids is utilized in Area 500 for energy production and the sugar-rich hydrolysate is used as carbon source for the production of succinic acid (SA) in Area 300.

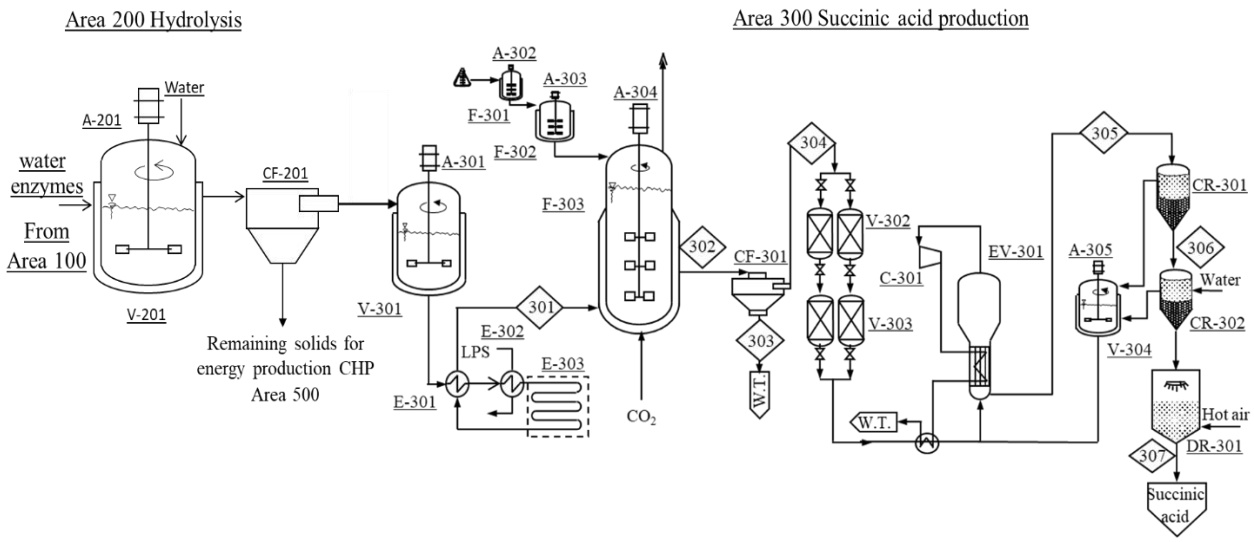
Area 300 is related to succinic acid production. The process starts with the mixing of nutrients, N-source and the hydrolysate from Area 200 in the mixing tank (V-301) followed by sterilization (E-301, E-302, E-303). For maximum bacterial performance to produce SA, the pH was maintained at 6.7 using 10 M NaOH. The fermented broth was centrifuged in centrifugal separator (CF-301) to separate the bacterial biomass. The biomass free broth was fed to active carbon columns (V-303, V-304) for de-colorization and impurity removal. The decolorized effluent was fed to cationic resin columns (V-305, V-306) in order to transform organic acid salts into their corresponding organic acids via acidification. The acidified liquid was concentrated using mechanical vapor recompression (MVR)-forced circulation evaporator system (EV-301). The concentrated liquid was supplied into continuous crystallizers (CR-301, CR-302) and the SA crystals were removed by rotary filter unit (RF-301, CF-302). The wet succinic acid crystals were dried in a spray dryer (DR-301).

In Area 400, the methanol-soluble lignin was mixed with epichlorohydrin (R-401). The water-soluble tetramethylammonium catalyst (TMAC) was added into the reactor, resulting in the opening of the epoxy ring and detaching the hydrogen chloride. Next, the epoxy ring was reconstructed with addition of sodium hydroxide. After the reaction, the organic layer was separated by decanting (D-401). The excess epichlorohydrin and organic solvent was distilled and recirculated. The distilled lignin epoxy resins is re-

dissolved (R-402) in methyl ethyl ketone (MEK) used as solvent. MEK was used because it can dissolve lignin epoxy resin whilst insoluble in water. This property of MEK is favorable to wash out NaCl produced as a byproduct during ring closure reaction leaving the final epoxidized product in the organic fraction.

In Area 500, the remaining organic solids (mainly Klason and acid soluble lignin), after hydrolysis step, are used to produce energy to cover part of the energy requirements of the total production process. This Area consists of a combined heat and energy production facility. The process starts by burning the organic solids with natural gas in the combustion chamber and the produced thermal energy used for steam production in boiler (B-501). The produced ultra-high pressure steam is fed to a steam turbine (T-501) which provides kinetic energy to an electricity generator (G-501).





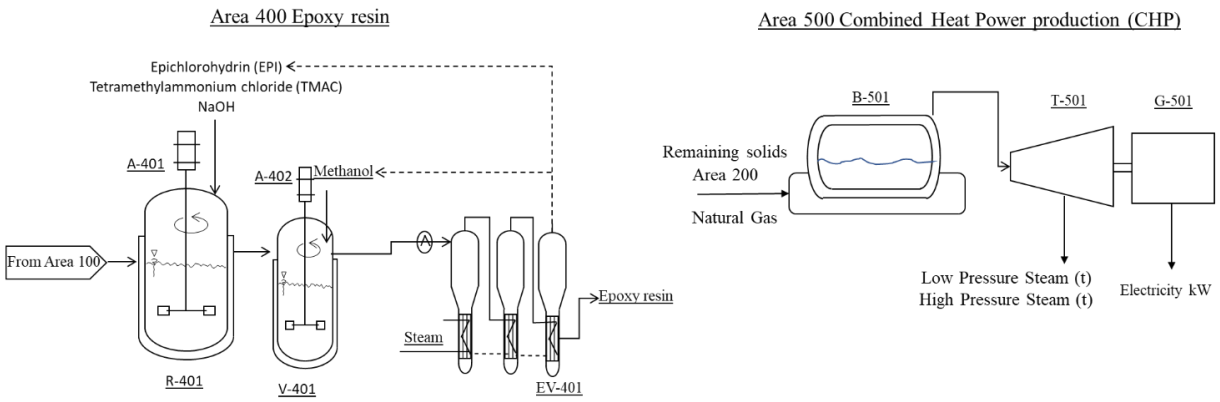


Figure 15. Process Flow Diagrams for Eucalyptus wood-based biorefinery for the production of epoxy resins and succinic acid.

5.2 Results – Techno-economic performance

Figure 16A presents the FCI of the whole process considering different plant capacities to produce both main products of epoxy resin and succinic acid. The FCI is decreased with increasing plant capacities due to the economies of scale up to a constant value. The highest FCI ($9.62/kg) was estimated at the lowest production capacity (10,000 t/year). Limited changes in the FCI values are observed above the threshold annual production capacity of 60,000 t/year where the FCI was observed at $5.32/kg. This annual production capacity was considered as the optimal plant capacity (OPC) for this process.

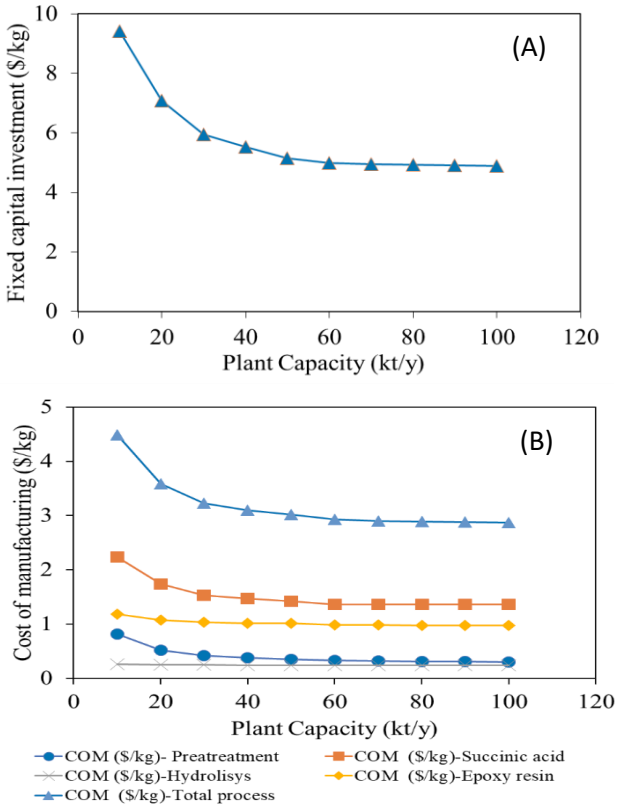


Figure 16. FCI (A) and COM (B) expressed per kg epoxy resin and estimated at different plant production capacities (10,000–100,000 t/year). COM is analyzed in the individual step processes of biomass pretreatment (AREA 100), Hydrolysis (AREA 200), Succinic acid production (AREA 300) and epoxy resin production (AREA 400).

The COM (Figure 16B) was estimated for the deferent process steps. The total COM was estimated at $2.92/kg of epoxy resin at the optimum plant capacity of 60,000 t/y. The succinic acid production contributes approximately 50% of the total COM and were estimated at $1.36/kg. The COM of the epoxy resin process itself estimated into $0.99/kg, were cost in the stages of pretreatment and hydrolysis estimated at $0.24/kg and $0.33/kg.

The MSP of epoxy resins (Figure 17) is estimated at varying plant production capacities and taking into consideration the revenues that can be obtained by selling all products of the developed biorefinery. The estimations are based on two different SA and antioxidants selling prices scenarios. At the first scenario the selling price of SA was $1700/t and for antioxidants $1000/t while at second was $1500/t and $500/t respectively. At optimum plant capacity of 60,000 t the MSP of epoxy resin is estimated at $0.14/kg for the first scenario and $0.91/kg the second.

The NPV was estimated at different plant capacities taking into consideration three different selling prices for epoxy resins $3000/t, $2500/t and $2000/t while the selling prices of SA was $1500/t and for antioxidants $500/t. NPV indicates positive values for capacities higher than 20,000 t, 30,000 t and 50,000 t for the epoxy resin selling pieces of $3000/t, $2500/t and $2000/t respectively. At optimum plant capacity the NPV is estimated at M$426, M$266 and M$36 and the Discounted Payback Period at 7, 9 and 18 years for the different selling prices for epoxy resins $3000/t, $2500/t and $2000/t respectively.

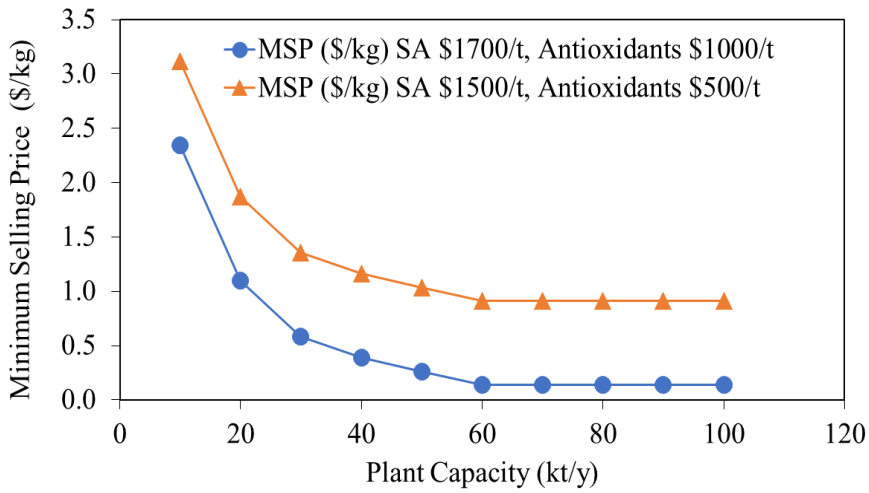


Figure 17. MSP of the epoxy resin at varying plant production capacities using different selling prices of the SA and Antioxidants. (▲) SA selling price of $1700/t and antioxidants $1000/t and (●) SA selling price of $1500/t and antioxidants $500/t.

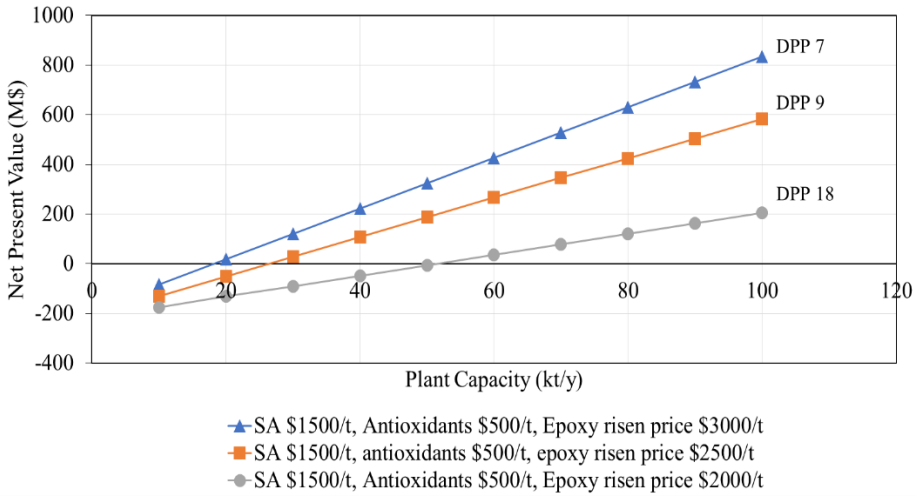


Figure 18. NPV at varying plant production capacities using different selling prices of the SA, Antioxidants, and epoxy resins. (▲) SA $1500/t; Antioxidants $500/t; and epoxy resins $3000/t, (■) SA $1500/t; Antioxidants $500/t; and epoxy resins $2500/t, (●) SA $1500/t; Antioxidants $500/t; and epoxy resins $2000/t.

5.3 Results – Environmental performance

The environmental performance of the bio-epoxy resins was evaluated using the LCA methodology. The LCA inventory was based on mass and energy balances derived from the process design. The inventory was expressed per kg of epoxy resins. The system boundaries includes Area 100 and Area 400, where mainly take place the pretreatment of biomass, the separation of the methanol lignin compounds and the process that related with the production epoxy resin. The GaBi software and its databases were used for the estimation of impact category indicators, which were actualized with CML 2001 methodology, while 1 kg of epoxy resins was used as functional unit. Finally, the environmental performance of the eucalyptus lignin epoxy resin is compared with the fossil-based counterpart with bisphenol.

Figure 19 presents the results of environmental impact indicators for eucalyptus lignin epoxy resin compared with the fossil-based counterpart with bisphenol, with the selected categories to be Global Warming Potential (GWP), Abiotic Depletion of fossil (ADP), Acidification Potential (AP), Eutrophication Potential (EP) and Human Toxicity (HT). The eucalyptus lignin epoxy resin indicates better environmental performance than the fossil derived counterpart. Specifically, the impact indicators of GWP, ADP and HT for the case of the bio-epoxy resin shows 46 %, 54% and 29 % lower values than the fossil epoxy resin, respectively.

The material and energy contribution to the environmental impact of bio-epoxy resin production is shown in Figure 20. The chemicals that are used for epoxy resin production step contribute the most to environmental impact. Among these, epichlorohydrin is the material which indicates the highest impact in all categories. The contributions of this material reached 55, 65 and 70% in indicators such as GWP, EP and AP respectively. The NaOH is the second most harmful material that involves 10% in case of the GWP, 5% on ADP and between 15-30% for the AP, EP and HT. The energy requirements of the production process is the another factor which contributes to the environmental impact. Steam represents 24% of GWP and 20% of the ADP while the natural gas 5% and 30%, respectively.

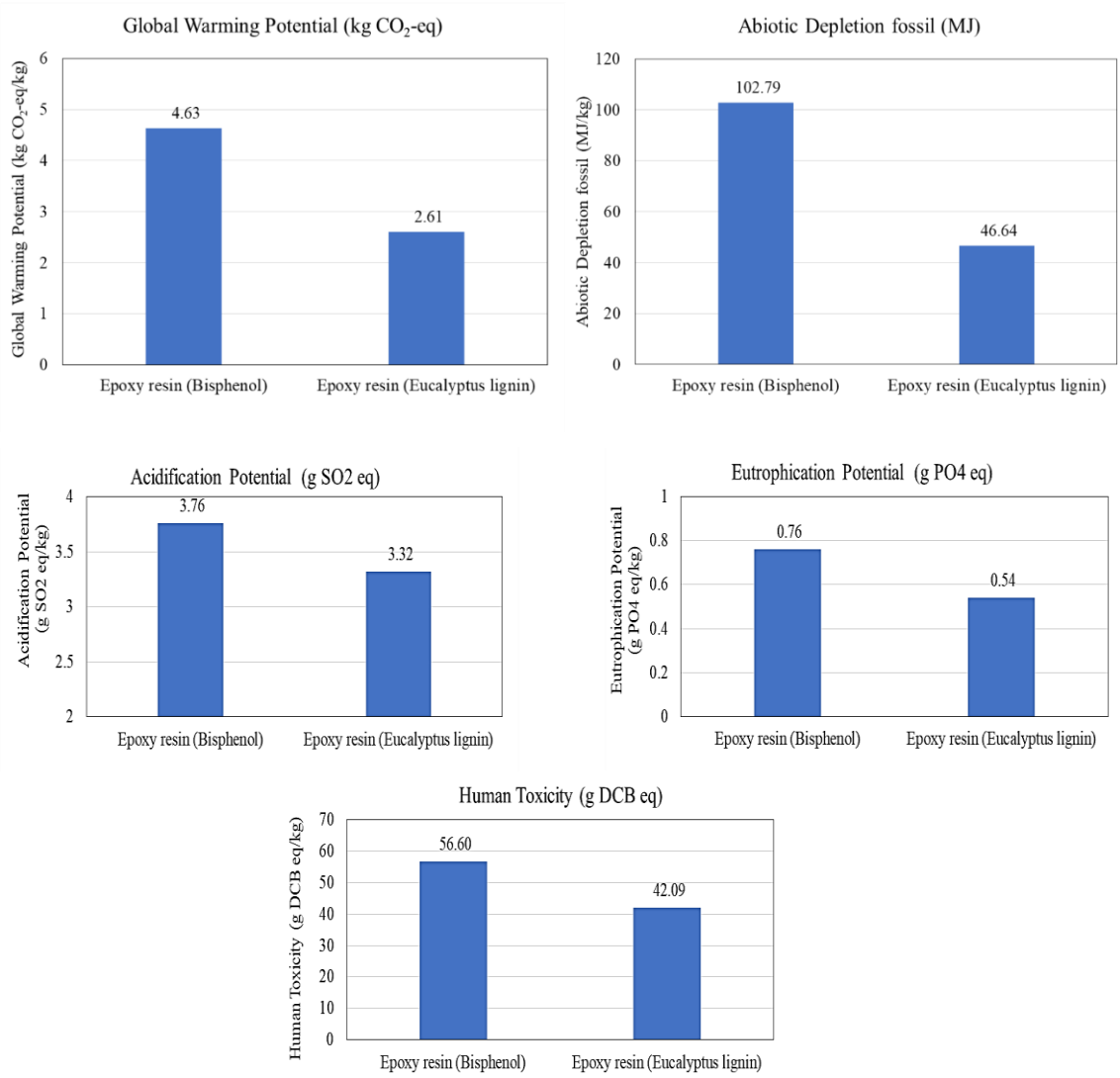


Figure 19. Environmental impact indicators for eucalyptus lignin-based epoxy resins production compared with the fossil-based counterpart with bisphenol

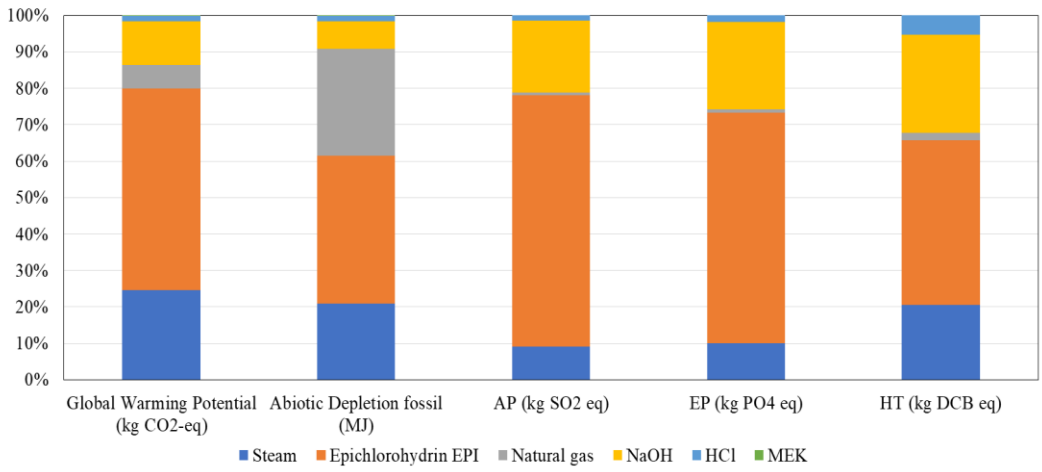


Figure 20. Contribution of the main materials and energy to environmental impact indicators for the production of bio-epoxy resin.

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