

# Techno-economic optimization of a process superstructure for lignin valorization

Ada Josefina Robinson<sup>a</sup>, Aristide Giuliano<sup>b\*</sup>, Omar Y. Abdelaziz<sup>c</sup>, Christian P. Hulteberg<sup>c</sup>,  
Apostolis Koutinas<sup>d</sup>, Konstantinos S. Triantafyllidis<sup>e</sup>, Isabella De Bari<sup>b</sup>, Diego Barletta<sup>a</sup>

<sup>a</sup> Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano (SA), Italy

<sup>b</sup> ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, S.S. 106 Ionica, laboratory Biorefineries and Green Chemistry, km 419+500, Rotondella (MT), Italy

<sup>c</sup> Department of Chemical Engineering, Lund University, Naturvetarvägen 14, SE-221 00 Lund, Sweden

<sup>d</sup> Department of Food Science and Human Nutrition, Agricultural University of Athens, Iera Odos 75, 118 55 Athens, Greece

<sup>e</sup> Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece

\*aristide.giuliano@enea.it

## Abstract

Lignin, the most abundant aromatic biopolymer on earth, is often considered a biorefinery by-product, despite its potential to be valorized into high-added-value chemicals and fuels. In this work, an integrated superstructure-based optimization model was set up and optimized for the technical lignins conversion to target products using mixed-integer non-linear programming. Three main biobased products were selected: aromatic monomers, phenol-formaldehyde resins, and aromatic aldehydes/acids. Furthermore, integrated process flowsheets and economic data were assessed comparing simultaneously several alternative conversion pathways to assess the profitability of lignins-based processes by predicting the performance of technologies with different TRL. Results highlighted technical lignins could have a market value of 200 €/t when the market price for aromatic monomers, resins, and vanillin is at least 2.0, 0.8, and 15.0 €/kg, respectively. When higher-quality lignins were considered, the

process optimization showed that the most profitable product was vanillin, produced by novel technologies (i.e., high-temperature electrolysis).

**Keywords** Aromatic monomers, Biorefinery, Lignin valorization, Modeling, Phenolic resins, Process optimization, Vanillin

### **Nomenclature**

*AA* aromatic aldehydes/acids

*AM* aromatic monomers

*BTEX* benzene/toluene/ethylbenzene/xylene

*Cs* current scenario

*DES* deep eutectic solvents

*G* guaiacyl

*H* hydroxyphenyl

*HAMs* high AM price scenario

*HDO* hydrodeoxygenation

*HL* hydrolysis lignin

*HTL* hydrothermal liquefaction

*HTE* high-temperature electrolysis

*IL* ionic liquids

*j* different stages

*k* technology options

*KL* kraft lignin

*LAAs* low AA price scenario

*LS* lignosulfonates

*MINLP* mixed-integer non-linear programming

*MLMP* maximum lignin market price

*M<sub>w</sub>* weight-average molecular weight

*MWL* milled wood lignin

*OL* organosolv lignin

*p* process parts

*PFR* phenol-formaldehyde resin

*PM* profit margin

*S* syringyl

*SEL* steam-explosion lignin

*SL* soda lignin

*TAC* total annual cost

## **1 Introduction**

Lignocellulosic biomass is characterized by extensive availability and abundance, and globally accounts for 200 billion tons (Haveren et al., 2008). Depending on the local availability, lignocellulosic biomass can add to the development of several value chains and contributes diversifying the energy sources supply (Zhu et al., 2020). Nonetheless, crude oil is still the primary resource for the production of organic chemicals and fuel, leading to a carbon imbalance on the planet (Mottaghi et al., 2022).

Lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin representing up to a 10–40% of the biomass dry weight (Ragauskas et al., 2014). Lignin is the largest source of renewable aromatics on Earth (Alherech et al., 2021). The units *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) form an

intricate and recalcitrant biopolymer thanks to the dehydrogenative polymerization. These units are cross-linked via Several kind of carbon-carbon and carbon-oxygen bonds are present in the lignin structure, about 50 % are represented by  $\beta$ -O-4' and 5-5' bonds, while  $\alpha$ -O-4, 5-5,  $\beta$ -5,  $\beta$ -1, dibenzodioxocin, spirodienone, and  $\beta$ - $\beta$  bonds appear with less frequency (about 20 %) (Arshanitsa et al., 2016). Numerous technical lignins are identified by relevant structural differences reflecting the use of diverse raw materials and various isolation processes (Zevallos Torres et al., 2020). Each method influences the distribution of the functional groups and the average molecular weight values of the isolated fractions.

Besides lignin from biorefinery plants, the pulp and paper industry produces substantial amounts of lignin, which account for about 1.3 Mton/year (Zevallos Torres et al., 2020). Presently, many plants based on biomass pretreatment and fractionation have been constructed around the world. In these plants, lignin is a side-stream product typically burnt to satisfy internal needs in terms of heat and electricity (Usmani et al., 2021). Furthermore, several investigations have proven that, in many cases, a surplus of energy can be achieved (Martinez-Hernandez et al., 2019), and this opens the way to develop integrated process layouts involving lignin co-valorization into value-added products and energy (Kim et al., 2021). Lignin-based BTX can be used as a replacement for BTX from petroleum as they are similar. BTX constitute 60% of the total aromatics in the market and 24% of the global petrochemical market (Hodásová et al., 2015). The utilization of the phenolic structure of lignin to produce phenols has been established based on the investigation of the latest

research. Kraft lignin typically replaces up to 40% of phenol content in phenolic resins (Ghorbani et al., 2016); higher yields were obtained for polyol and from organosolv lignin by depolymerization processes ( $\approx 50\%$ ) (Ou et al., 2021). Abdelaziz et al. (2020) presented a conceptual design by modeling, simulation, and analysis of oxidation processes using experimental data to obtain lignin-based vanillin, vanillic acid, and acetovanillone. Hence, functional materials, chemicals, and fuels can be obtained from lignin valorization as a substitute to petroleum-based processes (Sidiras et al., 2022).

Despite this potential, there are some fundamental obstacles with respect to lignin's full exploitation. The major challenge in lignin utilization is to achieve standardized streams with target molecular weight distributions and specific reactivity attributed to the different types of functional groups (Lan et al., 2018). Novel processes are, therefore, necessary to convert lignin in a selective, efficient, and sustainable way into bio-based products (Borsella et al., 2020).

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. 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.

## 2 Methods

A novel methodology has been implemented in this work to achieve the process optimization for lignin conversion. 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. 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 analyses with an economic objective were performed.

## 2.1 Lignin-based biorefinery superstructure

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<sup>-1</sup>). 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<sub>3</sub>H 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).

Each kind of these technical lignins and their relevant properties is meticulously described and available in a recent report published by IEA Bioenergy (Mastrolitti et al., 2021).

In Fig. 1, 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, high-temperature electrolysis (HTE) and deep eutectic solvent (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).

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. 2) (Ramos et al., 2019).

Table 3 shows a description of each process considered in the different stages of each lignin-based target product, and data input was obtained from several specific scientific references. 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  $p$ .

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.

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). An innovative solvent can be used to dissolve and transform the lignin by a low-energy process (100 °C): a Zn-based DES. 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).

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 (Fig. 4). 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<sub>2</sub> partial pressure are available.

The second process to produce vanillin is catalyzed oxidative depolymerization. This consists of treating lignin with molecular O<sub>2</sub> at 170 °C and 5 bar O<sub>2</sub> 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 HTE 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). Pulp 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 removal 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. 2.

## 2.2 Mathematical model formulation

### 2.2.1 Process superstructure optimization by mixed integer non-linear programming

*MINLP* refers to mathematical optimization systems containing continuous and discrete variables in non-linear relationships as objective function and/or the equality/disequality constraints. The optimal alternative process pathways of the superstructure are individuated using binary variables (Giuliano et al., 2016). The mathematical optimization strategy of the process superstructure was approached following the procedure explained in Galanopoulos et al. (2019). The mass and energy balance equations, sizing equations, capital and operating cost estimation equations, together an economic profitability objective function were considered.

### 2.2.2 Reactive lignin

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 ( $\beta$ -O-4,  $\beta$ - $\beta$ , 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.

### 2.2.3 Mass and energy balances

Considering the lignin quality as previously described (Section 2.2.2), all mass and energy balances were performed. In particular, Table 1 condenses all

process yields and main operating conditions that were assumed for each treatment path.

#### 2.2.4 Cost estimation

The capital and operating costs for all considered process pathways were estimated employing the correlations with the mass flow rate of the feed or the generated power suggested by Andersson et al. (2020) and Werhan (2013) (see supplementary material). The raw material (lignin) supply cost was calculated as:

$$C_L F_{L,IN} \quad (1)$$

where  $C_L$  is the lignin market price and  $F_{L,IN}$  is the lignin feedstock flowrate.

The model parameters applied in this work are given in Table 2. The size of the lignin biorefinery is an essential parameter in making 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 factory, the input flow rate to the plant was assumed 180 kt/y of dry lignin.

The process revenues result from multiplying the sales of the lignin products rate (final product stream obtained from stage  $j=3$  (purification) by their respective selling price (€/t). As a result, the profit margin (PM) is given by:

$$PM = AF_{3,AA}P_{AA} + F_{3,AM}P_{AM} + F_{3,PFR}P_{PFR} - TAC \quad (2)$$

where  $F_{3,AA}$ ,  $F_{3,AM}$ ,  $F_{3,PFR}$  represent the streams of AA, AM, and PFR, respectively;  $p_{AA}$ ,  $p_{AM}$ ,  $p_{PFR}$  are their corresponding product selling price, and  $TAC$ , the Total Annual Costs.

### 2.2.7 Economic profitability objective functions

The lignin-based biorefinery optimization problem aims at deciding which path to take through the superstructure and the relevant flows entering and leaving each layer by a simplified approach based on a *MINLP*, that maximizes an economic objective function: *MLMP*, which is defined as the maximum cost of dry lignin allowing a positive or null net profit from the biorefinery operations. the *MLMP*:

$$MLMP = \max C_L \quad (3)$$

To carry out the optimization and obtain feasible results, it was necessary to consider a constraint on the final profit margin by fixing it equal to zero:

$$PM = 0 \quad (4)$$

the choice of maximizing  $C_L$  is due to the aim of finding the optimal process pathway as a function of the lignin market price and finding threshold values corresponding to the choice of alternative process pathways.

## 3 Results

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.

The parameters presented in Section 2.2 were used to calculate the total costs and revenues associated with three different outlined product-selling-price

scenarios. 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 a possible grant to incentivize the production of bio-based AM. Values of *MLMP* lower than 50 €/t<sub>DRY</sub> were considered not realistic (Shen et al., 2019). The minimum market values for different technical lignins are displayed in Fig. 3 (dotted line): 250 €/t<sub>DRY</sub> for soda lignin (SL) and lignosulfonates (LS), 350 €/t<sub>DRY</sub> for kraft lignin (KL), 220 €/t<sub>DRY</sub> for hydrolysis lignin (HL), and 500 €/t<sub>DRY</sub> 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, as defined in Section 2.2.2, 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. 2. 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  $J_1 K_7$ ,  $J_2 K_4$  and  $J_3 K_4$  (in yellow), while for percentages of reactive lignin higher than 65%, the preferable process will be  $J_1 K_9$ ,  $J_2 K_5$  and  $J_3 K_4$  (in green). As for LAAs,  $J_1 K_{27}$ ,  $J_2 K_4$ , and  $J_3 K_4$  (in yellow) is also the best solution for low percentages of reactive lignin, whereas for higher percentages of reactive lignin,  $J_1 K_6$ ,  $J_2 K_2$  and  $J_3 K_2$  (in purple) is preferred. Eventually, when HAMs are considered,  $J_1 K_1$ ,  $J_2 K_3$  and  $J_3 K_1$  (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  $J_2 K_1$  (rather than  $J_2 K_3$ ).

From an economic perspective, data in Fig. 3 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, as assumed in the Section 2.2.2, 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 (Table 1). 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. 3).

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. 3 shows that a *MLMP* larger than 150 €/t<sub>DRY</sub> 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. 4a 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 €/t<sub>DRY</sub>, mainly due to the ethyl acetate consumption (291 €/t<sub>DRY</sub>) and electricity consumption (149 €/t<sub>DRY</sub>), with less significant investment costs (IC) (main treatment 10 €/t<sub>DRY</sub>, upgrading 8 €/t<sub>DRY</sub>, and purification 2 €/t<sub>DRY</sub>).

From Fig. 4.b it can be seen that the yield to AA is only 5%. Nevertheless, revenues for these conditions are 754 €/t<sub>DRY</sub> with a profit margin of 275 €/t<sub>DRY</sub>, which can be derived from the inspection of the histograms outlined in Fig. 4a 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.

Related to resins production, the OC are slightly higher than the previous case, 496 €/t<sub>DRY</sub>. The most significant cost contributions are solvent consumption (170 €/t<sub>DRY</sub>) and maintenance (118 €/t<sub>DRY</sub>) due to the DES make-up cost. In addition, significant IC are significant (main treatment 55 €/t<sub>DRY</sub>, upgrading 64 €/t<sub>DRY</sub>), again attributed to the expensive main treatment, dissolution in DES, which is still an emerging technology (Fig. 4a). As can be seen in Fig. 4b, the yield to PFR was around 73%. With a selling price of 0.8 €/kg and revenues of 582 €/t<sub>DRY</sub>, the profit margin is only 86 €/t<sub>DRY</sub>. 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 €/t<sub>DRY</sub>, mainly due to utilities, 118 €/t<sub>DRY</sub>. Revenues are high in this optimistic scenario towards AA (256 €/t<sub>DRY</sub>), 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 catalysed 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. Recyng 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 (see supplementary material).

### 3.1 Discussion

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. 3). 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 Bbosa et al. (2018); 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 A. 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. 4b), 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-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, how to relate the specific lignin reactivity (Section 2.2.2) 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.

#### **4. Conclusions**

The techno-economic feasibility of lignin conversion into AM, PFR, and AA has been assessed for a plant scale of 150 kt/y, using a process superstructure solved by an *MINLP* approach. Each process pathway was modeled to be simultaneously compared, individuating the optimal flowsheet and its more profitable lignin-derived product. Different lignin feedstocks were considered by the introduction of different reactivity indexes. Vanillin resulted the best lignin-based product. Aromatic monomers, produced by hydrothermal liquefaction, are preferred when the quality of lignin is low, and the product selling price is at least 2.0 €/kg.

E-supplementary data for this work can be found in e-version of this paper online

## Acknowledgements

This work was performed in cooperation with ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) as a part of a broader network for joint actions on lignin with IEA Bioenergy Task 42 – Biorefining in a Circular Economy (<https://task42.ieabioenergy.com/>), LignoCOST (<https://lignocost.eu/>). The contribution of COST Action LignoCOST (CA17128), supported by COST (European Cooperation in Science and Technology), in promoting interaction, exchange of knowledge and collaboration in the field of lignin valorization is gratefully acknowledged.

## CRedit author statement

**Ada Josefina Robinson:** Methodology, Software, Validation, Investigation, Writing - Original Draft, Visualization. **Aristide Giuliano:** Conceptualization, Methodology, Software, Formal analysis, Data curation, Writing - Review & Editing, Visualization, Project administration. **Omar Y. Abdelaziz:** Conceptualization, Methodology, Writing - Review & Editing, Project administration. **Christian P. Hulteberg:** Methodology, Writing - Review & Editing, Supervision, Funding acquisition. **Apostolis Koutinas:** Methodology, Writing - Review & Editing, Funding acquisition. **Konstantinos S. Triantafyllidis:** Conceptualization, Methodology, Writing - Review & Editing. **Isabella De Bari:** Conceptualization, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition. **Diego Barletta:** Conceptualization, Methodology, Software, Writing - Review & Editing, Supervision.

## Declaration of competing interest

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. **References**

1. Abdelaziz, O.Y., Al-Rabiah, A.A., El-Halwagi, M.M., Hulteberg, C.P., 2020. Conceptual Design of a Kraft Lignin Biorefinery for the Production of Valuable Chemicals via Oxidative Depolymerization. *ACS Sustainable Chem. Eng.* 8, 8823–8829. <https://doi.org/10.1021/acssuschemeng.0c02945>
2. Alherech, M., Omolabake, S., Holland, C.M., Klinger, G.E., Hegg, E.L., Stahl, S.S., 2021. From Lignin to Valuable Aromatic Chemicals: Lignin Depolymerization and Monomer Separation via Centrifugal Partition Chromatography. *ACS Cent. Sci.* 7, 1831–1837. <https://doi.org/10.1021/acscentsci.1c00729>
3. Andersson, L., Hallbeck, J., Lancaster, T., Guan, J., , 2020. Feasibility study of lignin valorisation at Södra Cell in Mörrum. Lund University.
4. Arshanitsa, A., Krumina, L., Telysheva, G., Dizhbite, T., 2016. Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis. *Industrial Crops and Products* 92, 1–12. <https://doi.org/10.1016/j.indcrop.2016.07.050>
5. Azadi, P., Inderwildi, O.R., Farnood, R., King, D.A., 2013. Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renewable and Sustainable Energy Reviews* 21, 506–523. <https://doi.org/10.1016/j.rser.2012.12.022>
6. Borsella, E., De Bari, I., Colucci, P., Mastrolitti, S., Liuzzi, F., De Stefanis, A., Valentini, V., Gallese, F., Perez, G., 2020. Lignin Depolymerization by Catalytic Hydrodeoxygenation Performed with Smectitic Clay-Based Materials. *Energy Technology* 8. <https://doi.org/10.1002/ente.202000633>
7. Cao, Y., Chen, S.S., Zhang, S., Ok, Y.S., Matsagar, B.M., Wu, K.C.-W., Tsang, D.C.W., 2019. Advances in lignin valorization towards bio-based chemicals and fuels: Lignin biorefinery. *Bioresource Technology* 291, 121878. <https://doi.org/10.1016/j.biortech.2019.121878>
8. Constant, S., Basset, C., Dumas, C., Di Renzo, F., Robitzer, M., Barakat, A., Quignard, F., 2015. Reactive organosolv lignin extraction from wheat straw: Influence of Lewis acid catalysts on structural and chemical properties of lignins. *Industrial Crops and Products* 65, 180–189. <https://doi.org/10.1016/j.indcrop.2014.12.009>
9. Dornelles, L.B., Filho, R.M., Mariano, A.P., 2021. Organosolv fractionation of eucalyptus: Economics of cellulosic ethanol and chemicals versus lignin valorization to phenols and polyols. *Industrial Crops and Products* 173, 114097. <https://doi.org/10.1016/j.indcrop.2021.114097>
10. Galanopoulos, C., Giuliano, A., Barletta, D., Zondervan, E., 2020. An integrated methodology for the economic and environmental assessment

- of a biorefinery supply chain. *Chemical Engineering Research and Design* 160, 199–215. <https://doi.org/10.1016/j.cherd.2020.05.016>
11. Galanopoulos, C., Kenkel, P., Zondervan, E., 2019. Superstructure optimization of an integrated algae biorefinery. *Computers & Chemical Engineering* 130, 106530. <https://doi.org/10.1016/j.compchemeng.2019.106530>
  12. Ghorbani, M., Liebner, F., Van Herwijnen, H.W.G., Pfungen, L., Krahofer, M., Budjav, E., Konnerth, J., 2016. Lignin Phenol Formaldehyde Resoles: The Impact of Lignin Type on Adhesive Properties. *BioResources* 11, 6727–6741. <https://doi.org/10.15376/biores.11.3.6727-6741>
  13. Giuliano, A., Cerulli, R., Poletto, M., Raiconi, G., Barletta, D., 2016. Process Pathways Optimization for a Lignocellulosic Biorefinery Producing Levulinic Acid, Succinic Acid, and Ethanol. *Ind. Eng. Chem. Res.* 55, 10699–10717. <https://doi.org/10.1021/acs.iecr.6b01454>
  14. Giuliano, A., Cerulli, R., Poletto, M., Raiconi, G., Barletta, D., 2014. Optimization of a Multiproduct Lignocellulosic Biorefinery using a MILP Approximation, in: *Computer Aided Chemical Engineering*. Elsevier, pp. 1423–1428. <https://doi.org/10.1016/B978-0-444-63455-9.50072-6>
  15. Haveren, J. van, Scott, E.L., Sanders, J., 2008. Bulk chemicals from biomass. *Biofuels, Bioprod. Bioref.* 2, 41–57. <https://doi.org/10.1002/bbb.43>
  16. Hodášová, L., Jablonsky, M., Butor Skulcova, A., Haz, A., 2015. Lignin, potential products and their market value. *Wood research* 60, 973–986.
  17. Hong, S., Sun, X., Lian, H., Pojman, J.A., Mota-Morales, J.D., 2020. Zinc chloride/acetamide deep eutectic solvent-mediated fractionation of lignin produces high- and low-molecular-weight fillers for phenol-formaldehyde resins. *J Appl Polym Sci* 137, 48385. <https://doi.org/10.1002/app.48385>
  18. Kalami, S., Arefmanesh, M., Master, E., Nejad, M., 2017. Replacing 100% of phenol in phenolic adhesive formulations with lignin. *J. Appl. Polym. Sci.* 134, 45124. <https://doi.org/10.1002/app.45124>
  19. Khwanjaisakun, N., Amornraksa, S., Simasatitkul, L., Charoensuppanimit, P., Assabumrungrat, S., 2020. Techno-economic analysis of vanillin production from Kraft lignin: Feasibility study of lignin valorization. *Bioresource Technology* 299, 122559. <https://doi.org/10.1016/j.biortech.2019.122559>
  20. Kim, H., Lee, S., Lee, J., Won, W., 2021. Simultaneous production of 1,6-hexanediol, furfural, and high-purity lignin from white birch: Process integration and techno-economic evaluation. *Bioresource Technology* 331, 125009. <https://doi.org/10.1016/j.biortech.2021.125009>
  21. Lan, W., Yue, F., Rencoret, J., del Río, J., Boerjan, W., Lu, F., Ralph, J., 2018. Elucidating Tricin-Lignin Structures: Assigning Correlations in HSQC Spectra of Monocot Lignins. *Polymers* 10, 916. <https://doi.org/10.3390/polym10080916>
  22. Laurichesse, S., Avérous, L., 2014. Chemical modification of lignins: Towards biobased polymers. *Progress in Polymer Science* 39, 1266–1290. <https://doi.org/10.1016/j.progpolymsci.2013.11.004>
  23. Martinez-Hernandez, E., Cui, X., Scown, C.D., Amezcua-Allieri, M.A., Aburto, J., Simmons, B.A., 2019. Techno-economic and greenhouse gas

- analyses of lignin valorization to eugenol and phenolic products in integrated ethanol biorefineries. *Biofuels, Bioprod. Bioref.* 13, 978–993. <https://doi.org/10.1002/bbb.1989>
24. Mastrolitti, S., Borsella, E., Giuliano, A., Petrone, M.T., Bari, I.D., Gosselink, R., van Erven, G., Annevelink, E., Triantafyllidis, K.S., Stichnothe, H., 2021. Sustainable lignin valorization 195 ISBN: 979-12-80907-01-1. <https://doi.org/ISBN: 979-12-80907-01-1>
  25. Mottaghi, M., Bairamzadeh, S., Pishvae, M.S., 2022. A taxonomic review and analysis on biomass supply chain design and planning: New trends, methodologies and applications. *Industrial Crops and Products* 180, 114747. <https://doi.org/10.1016/j.indcrop.2022.114747>
  26. Paysepar, H., Hu, Y., Feng, S., Yuan, Z., Shui, H., Xu, C. (Charles), 2020. Bio-phenol formaldehyde (BPF) resoles prepared using phenolic extracts from the biocrude oils derived from hydrothermal liquefaction of hydrolysis lignin. *Reactive and Functional Polymers* 146, 104442. <https://doi.org/10.1016/j.reactfunctpolym.2019.104442>
  27. Ragauskas, A.J., Beckham, G.T., Biddy, M.J., Chandra, R., Chen, F., Davis, M.F., Davison, B.H., Dixon, R.A., Gilna, P., Keller, M., Langan, P., Naskar, A.K., Saddler, J.N., Tschaplinski, T.J., Tuskan, G.A., Wyman, C.E., 2014. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* 344, 1246843. <https://doi.org/10.1126/science.1246843>
  28. Ramos, F.D., Delpino, C.A., Villar, M.A., Diaz, M.S., 2019. Design and optimization of poly(hydroxyalkanoate)s production plants using alternative substrates. *Bioresource Technology* 289, 121699. <https://doi.org/10.1016/j.biortech.2019.121699>
  29. Shen, R., Tao, L., Yang, B., 2019. Techno-economic analysis of jet-fuel production from biorefinery waste lignin. *Biofuels, Bioprod. Bioref.* 13, 486–501. <https://doi.org/10.1002/bbb.1952>
  30. Sidiras, D., Politi, D., Giakoumakis, G., Salapa, I., 2022. Simulation and optimization of organosolv based lignocellulosic biomass refinery: A review. *Bioresource Technology* 343, 126158. <https://doi.org/10.1016/j.biortech.2021.126158>
  31. Usmani, Z., Sharma, M., Awasthi, A.K., Lukk, T., Tuohy, M.G., Gong, L., Nguyen-Tri, P., Goddard, A.D., Bill, R.M., Nayak, S.C., Gupta, V.K., 2021. Lignocellulosic biorefineries: The current state of challenges and strategies for efficient commercialization. *Renewable and Sustainable Energy Reviews* 148, 111258. <https://doi.org/10.1016/j.rser.2021.111258>
  32. Vural Gursel, I., Dijkstra, J.W., Huijgen, W.J.J., Ramirez, A., 2019. Techno-economic comparative assessment of novel lignin depolymerization routes to bio-based aromatics. *Biofuels, Bioprod. Bioref.* 13, 1068–1084. <https://doi.org/10.1002/bbb.1999>
  33. Walch, F., Abdelaziz, O.Y., Meier, S., Bjelić, S., Hultberg, C.P., Riisager, A., 2021. Oxidative depolymerization of Kraft lignin to high-value aromatics using a homogeneous vanadium–copper catalyst. *Catal. Sci. Technol.* 11, 1843–1853. <https://doi.org/10.1039/D0CY02158J>
  34. Wang, B., Gebreslassie, B.H., You, F., 2013. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated

- life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Computers & Chemical Engineering* 52, 55–76. <https://doi.org/10.1016/j.compchemeng.2012.12.008>
35. Werhan, H., 2013. A process for the complete valorization of lignin into aromatic chemicals based on acidic oxidation. ETH Zurich. <https://doi.org/10.3929/ETHZ-A-009790818>
36. Wongtanyawat, N., Lusanandana, P., Khwanjaisakun, N., Kongpanna, P., Phromprasit, J., Simasatitkul, L., Amornraksa, S., Assabumrungrat, S., 2018. Comparison of different kraft lignin-based vanillin production processes. *Computers & Chemical Engineering* 117, 159–170. <https://doi.org/10.1016/j.compchemeng.2018.05.020>
37. Zevallos Torres, L.A., Lorenci Woiciechowski, A., de Andrade Tanobe, V.O., Karp, S.G., Guimarães Lorenci, L.C., Faulds, C., Soccol, C.R., 2020a. Lignin as a potential source of high-added value compounds: A review. *Journal of Cleaner Production* 263, 121499. <https://doi.org/10.1016/j.jclepro.2020.121499>
38. Zhu, P., Abdelaziz, O.Y., Hulteberg, C.P., Riisager, A., 2020. New synthetic approaches to biofuels from lignocellulosic biomass. *Current Opinion in Green and Sustainable Chemistry* 21, 16–21. <https://doi.org/10.1016/j.cogsc.2019.08.005>
39. Zirbes, M., Quadri, L.L., Breiner, M., Stenglein, A., Bomm, A., Schade, W., Waldvogel, S.R., 2020. High-Temperature Electrolysis of Kraft Lignin for Selective Vanillin Formation. *ACS Sustainable Chem. Eng.* 8, 7300–7307. <https://doi.org/10.1021/acssuschemeng.0c00162>

## Figures captions

Fig. 1. Different lignin valorization techniques and their main highlights and challenges.

Fig. 2. Optimal flowsheets obtained from the superstructure by maximizing the objective function.

Fig. 3. 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, liginosulfonates; SL, soda lignin; HL, hydrolysis lignin)

Fig. 4. (a) Production cost distribution and product sales revenues; (b) Yields, purity, and recovery rates of vanillin during valorization.

## Tables

Table 1

Operating conditions and yields of products for main treatment stages

(Abdelaziz et al., 2020; Gursel et al., 2019; Hong et al., 2020; Kalami et al., 2017; Walch et al., 2021; Zirbes et al., 2020).

Transformation process	Component	Yield (% of lignin)	$T$ (°C)	$P$ (bar)
HTL	Reactive lignin	27	250/350	40/20
	Phenol	3		
	Gases	3		
	Acids	21		
	Cresol	5		
	Catechol	10		
	BTX	0		
Pyrolysis	Reactive Lignin	7		1
	Gases	17		
	Acids	18		
	Cresol	0		
	Catechol	0		
	BTX	14%		
HDO	Reactive Lignin	2	400	150
	Phenol	23		
	Gases	7		
	Acids	41		
	Cresol	0		
	Catechol	1		
	BTX	7		

DES	Reactive lignin	73	100	1
	Biooil	0		
PF synthesis	PFR	71	80	1
Oxidative depolymerization	Vanillin	1.25	160	8.5
	Vanillic acid	0.97		
	Formic acid	3.73		
	Acetic acid	1.36		
	Guaiacol	0.67		
	Acetovanillone	0.30		
Catalyzed oxidative depolymerization	Vanillin	3.70	170	5
	Vanillic acid	3.10		
	Acetovanillone	0.90		
HTE	Vanillin	3.00	160	8
	Vanillic acid	2.33		
	Acetovanillone	0.76		

Table 2

Costs of chemicals, solvents, reactants and process parameters considered in the economic analysis.

Model parameter/component	Unit	Value
Dry lignin feedstock	t/y	180000
Operating hours per year	h/y	7200
Capital recovery factor	–	0.16
Wastewater purification cost	€/t	0.53
Project lifetime	y	20
Phenol	€/t	1080
NaOH	€/t	149
H <sub>2</sub>	€/t	3000
EtOH	€/t	500
ZnCl <sub>2</sub>	€/t	800
H <sub>2</sub> SO <sub>4</sub>	€/t	81
Formaldehyde	€/t	600
Ethyl acetate	€/t	1016
Oxidation catalyst	€/t	34000
O <sub>2</sub>	€/t	177.9

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 <sub>2</sub>	(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., 2019)
			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	(Abdelaziz et al., 2020)
3	4	AA	Distillation columns	
3	5	AA	Adsorption by resins	(Wang et al., 2013)

## Figures

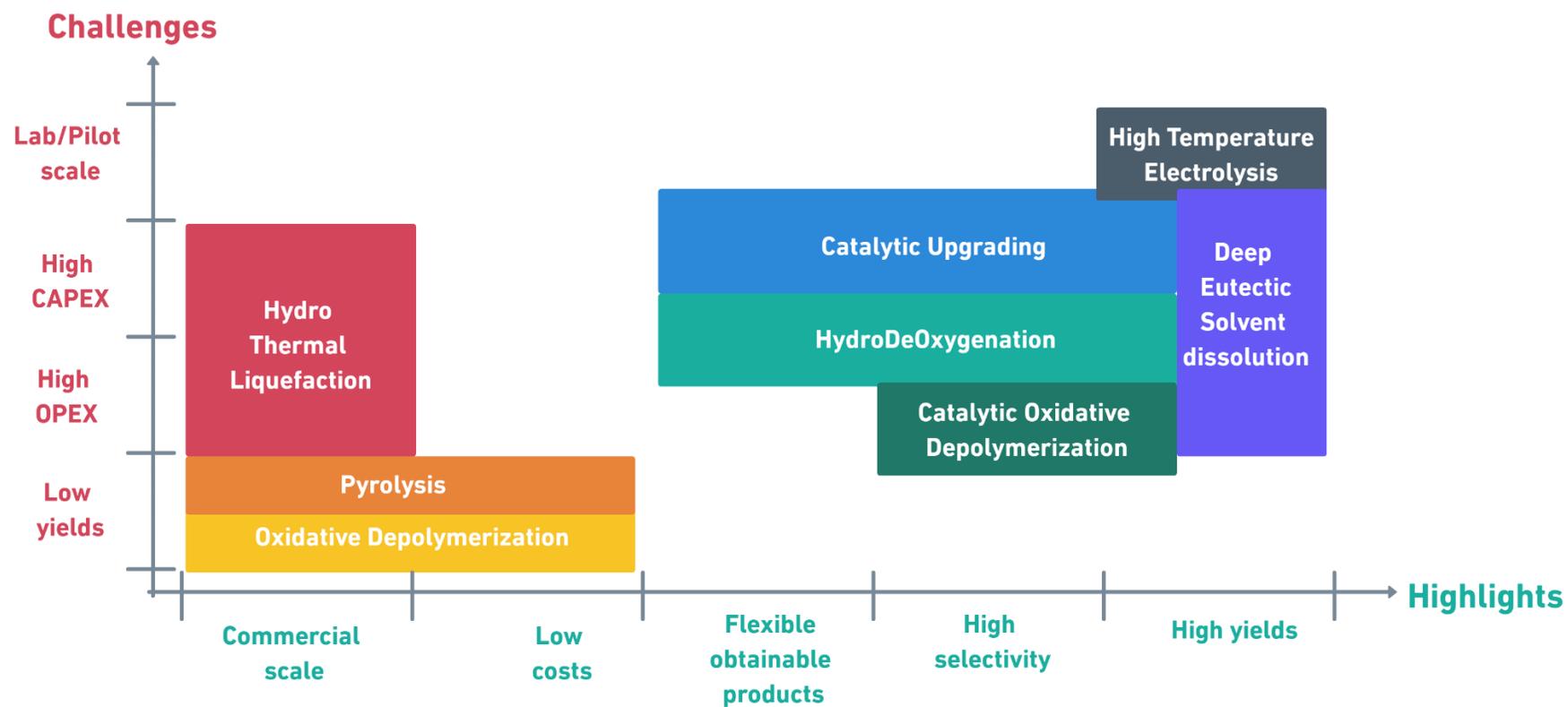


Fig. 1

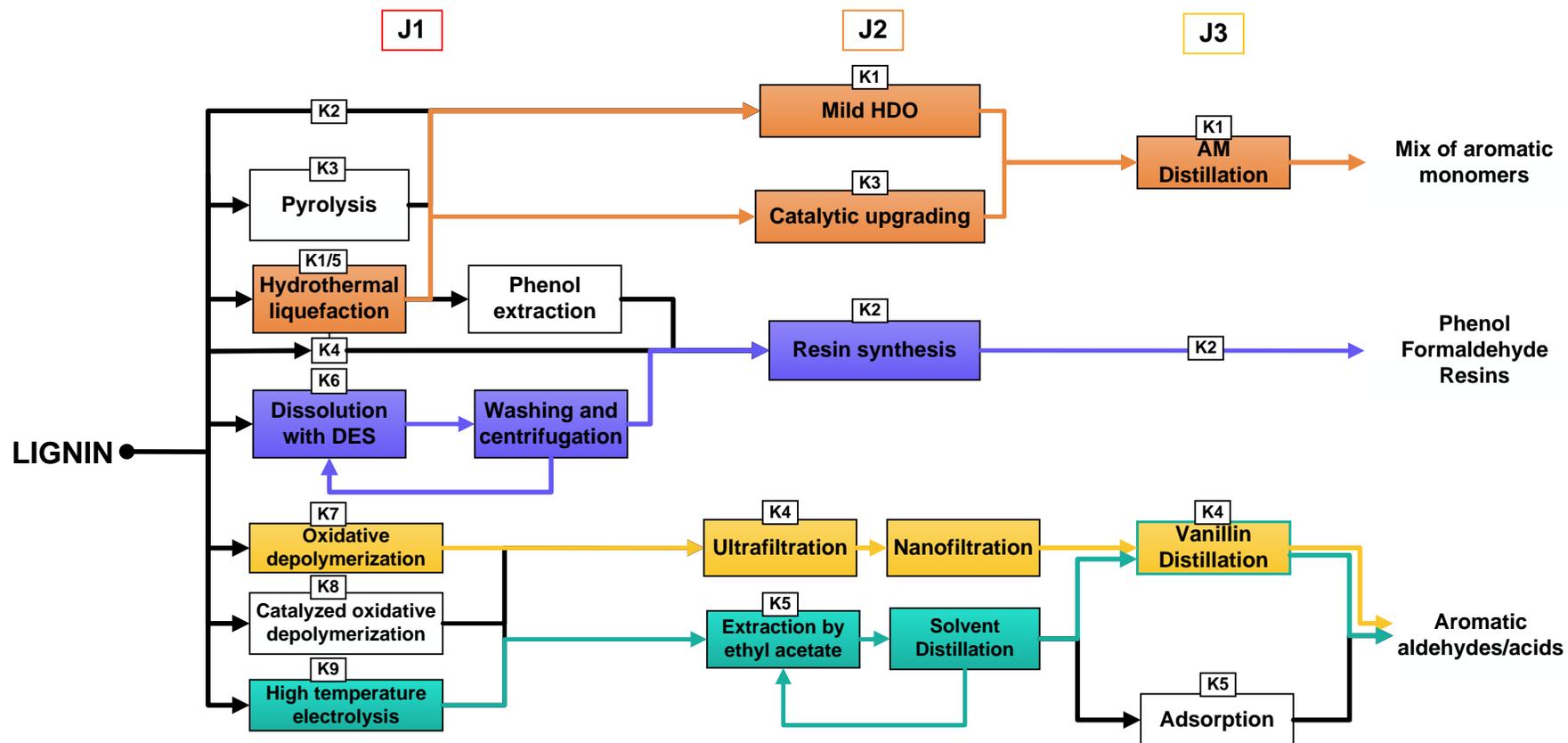


Fig. 2

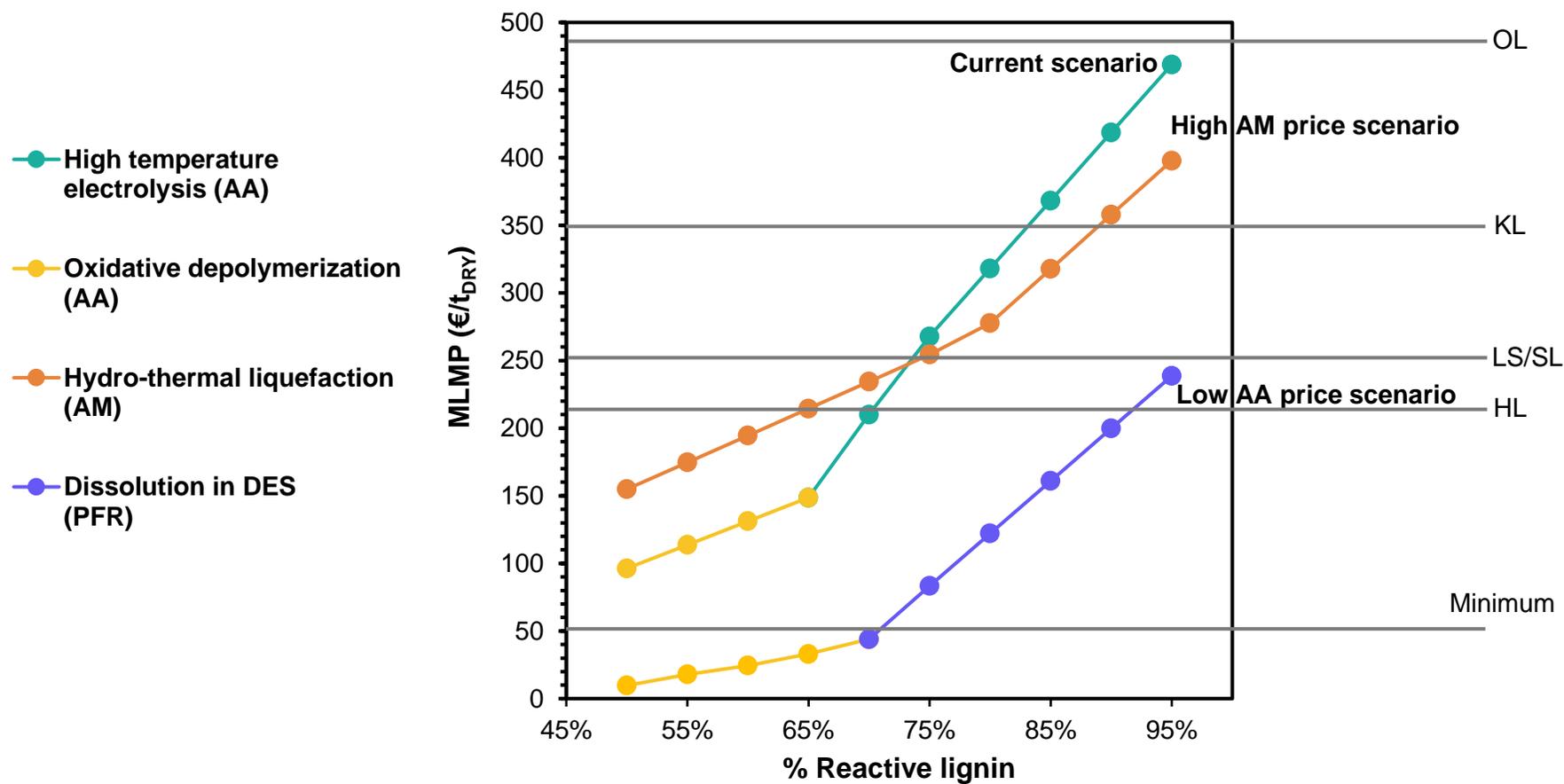


Fig. 3

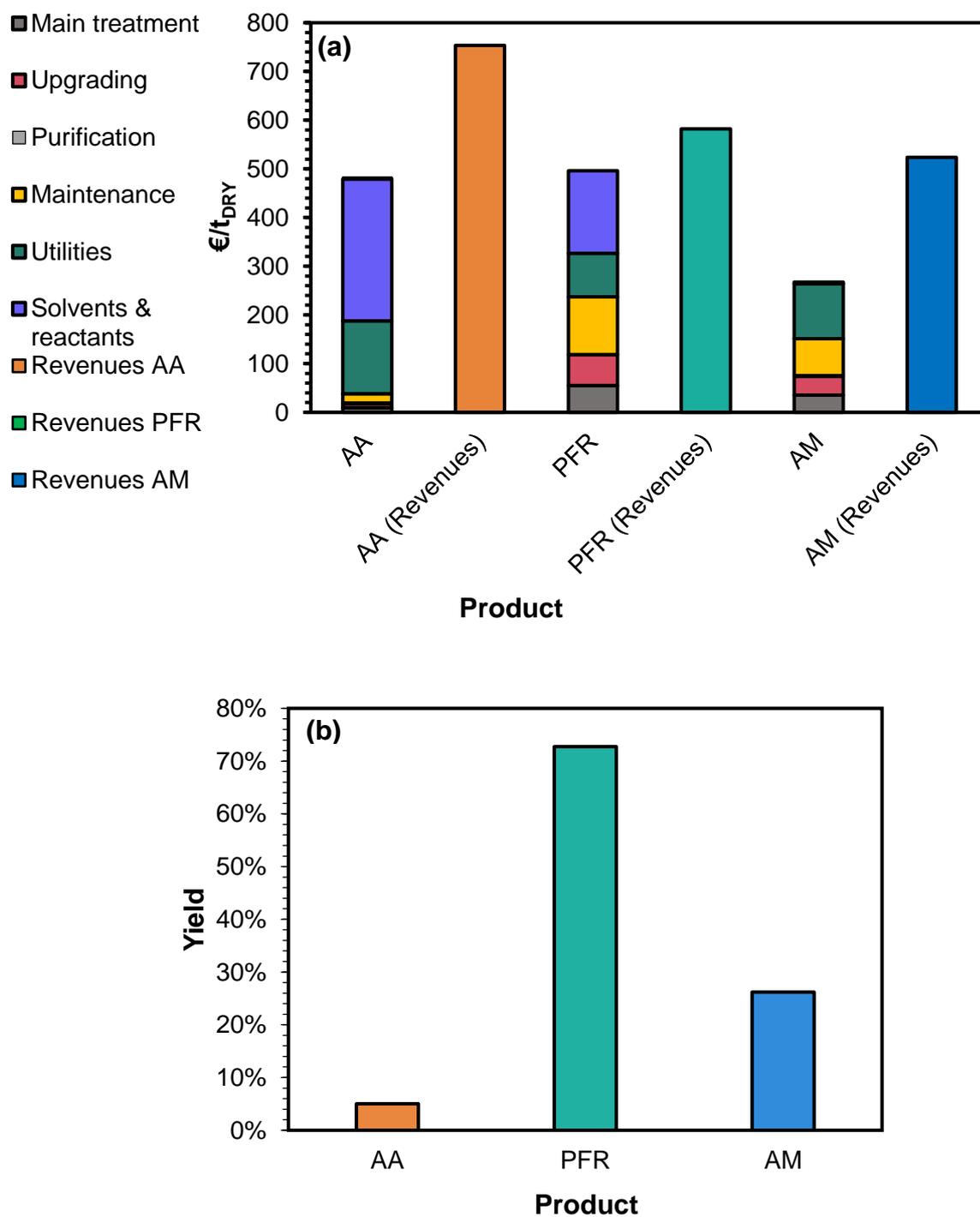


Fig. 4 (a) and (b)