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Optimization of a Lignin Valorization Process Superstructure using a MILP Approach

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Lignocellulosic biomass, including both herbaceous and woody feedstock, is currently widely used in many biorefineries. The lignin fraction (20-35 $\%_{DRY}$) is typically thermochemically converted into the cogeneration section of the biorefinery to produce heat and electricity. However, lignin holds a greater potential in several industrial sectors to produce biobased materials and several chemical building blocks. In particular, novel technologies allow obtaining low molecular weight compounds, such as aromatic or hydrocarbons. In this work, a mathematical methodology was developed to evaluate the best option in terms of lignin valorization. A process superstructure was built to compare alternative process pathways from lignocellulosic biomass. The following conversion options were considered: jet-fuels (JF), phenol-formaldehyde resins (PFR), polyurethane foams (PUF), and syngas for green electricity generation. By AIMMS optimization software, a Mixed Integer Linear Programming (MILP) was applied to obtain a simplified mathematical analysis and, consequently, the maximum lignin cost maximization for each lignin valorization process. In particular, process conversion, required utilities, product values were assessed for each process technology. Preliminary results show that the production of phenol-formaldehyde resins is the process closer to the market uptake. On the other side, polyurethane and jet-fuels appear still far from the market and their production would be feasible at a polyurethane foams and jet-fuel selling price at 300 % of the current selling price.

1. Introduction

The increasing ratio between the worldwide demand for fuels and chemicals and the number of petroleum reserves and the planned reduction of greenhouse gas emissions are fostering the development of non-petroleum based processes (Migliori et al., 2019). In this framework, lignocellulosic-based biorefineries are considered promising industrial models to produce biofuels for transportation and several added-value chemicals (Giuliano et al., 2019b). The main biomass components are cellulose (30-50 $\%_{DRY}$), hemicellulose (20-30 $\%_{DRY}$) and lignin (20-35 $\%_{DRY}$). Biomass pretreatment and fractionation can be implemented through different technologies based on chemical, physicochemical and biological processes. The resulting lignin is typically considered a side stream and it is thermochemically converted in the cogeneration section of the biorefinery to produce heat and electricity. However, lignin holds a greater potential in several industrial sectors to produce biobased materials and several chemical building blocks (Oliveira et al., 2019). The structure and composition of lignins can be very variable. Furthermore, Kraft lignin is the most widespread in the world, lignins derived from biorefinery processes (e.g., Organosolv lignins) are very promising in terms of future availability and composition. A comparison between Kraft lignin and Organosolv lignin can help to give directions to industrial and scientific stakeholders in the biorefining field. A huge research effort has been devoted to identifying the more convenient lignin conversion technologies. In particular, novel technologies allow obtaining low molecular weight compounds, such as aromatic or cyclic hydrocarbons. The main challenge is to develop novel processes able to convert lignin in a selective, efficient and sustainable way to biobased products. For the latter issue, the optimization of process synthesis and integration can help to identify the most promising pathways and to increase the profitability of the process. Process synthesis

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methods have been widely used in the conceptual design and optimization of sustainable and cost-effective bioethanol production plants (Giuliano et al., 2019a). The process synthesis is based on mathematical programming. A systematic methodology of mathematical programming consists of discrete/continuous optimization problems referred to as Mixed Integer Non-Linear Programming (MINLP) problems. Several authors considered different methods of process optimization (Zondervan et al., 2011) like disjunctive programming (Ponce-Ortega et al., 2012) and MINLP problem solution (Belmonte et al., 2019). In all these cases, the authors identified the best process pathways among the available alternatives or the best end products to maximize a techno-economic objective function. However, only a few works addressed the optimization of the lignin valorization among alternative pathways. Lignin-derived products include phenol-formaldehyde resins (PFR) (Kalami et al., 2017) or polyurethane foams (PUF) (Mahmood et al., 2014), jet-fuels (JF) (Shimanskaya et al., 2019) or energy production through the intermediate syngas generation (SG) (Pinto et al., 2015). In this paper, a simplified approach based on Mixed Integer Linear Programming is presented and applied to find an approximate solution of the non-linear problem of the economic optimization of a lignin-based biorefinery. In particular, the production of energy through syngas, jet-fuels, phenol-formaldehyde resins, polyurethane foams were studied. The aim of the work is the assessment of the optimal process pathway, varying some parameter values and the kind of lignin used as feedstock (Kraft lignin or Organosolv lignin).

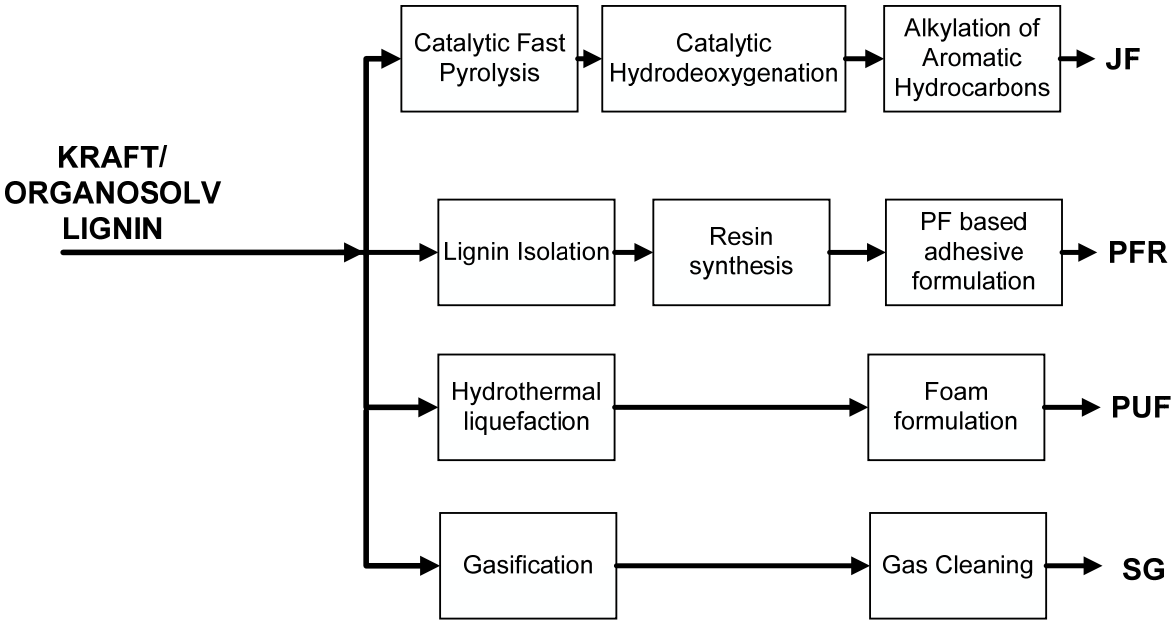

Figure 1: Superstructure of the lignin-based biorefinery

2. Lignin-based biorefinery superstructure

After an accurate literature survey of the most commonly used pathways, a superstructure of the lignin-based biorefinery was built. The biorefinery superstructure consists of four possible processes (Figure 1) to produce four different products:

JF) jet-fuels production by fast pyrolysis, catalytic hydrodeoxygenation and alkylation processes.

Lignin to be fed to the fast pyrolysis reactor has to be dried. The fast pyrolysis reactor (650 °C) transforms the lignin to three different intermediate products: biochar, syngas and bio-oil. The liquid fraction (bio-oil) is converted by the catalytic hydrodeoxygenation reactor at 320 °C and 170 bar. The final production of the jet-fuels carries out by the alkylation reactor at 220 °C and 35 bar (Cheng and Brewer, 2017).

PFR) phenol-formaldehyde resins production by lignin isolation and resins synthesis and formulation processes. NaOH is added to the pretreated biomass to dissolve the lignin, H_2SO_4 is added to the solution after this step to obtain the precipitation of lignin fraction. Formaldehyde (37 %wt) is used in the synthesis reactor using NaOH as catalysts at 85 °C. The final formulation of the PFR carries out by adding wheat flour and alder bark modal (Kalami et al., 2017).

PUF) polyurethane foams production by hydrothermal liquefaction and foam formulation processes. A 50/50 water/ethanol solution is used for the hydrothermal liquefaction of lignin at 25 bar and 250 °C. After this step, the final foam formulation is achieved by adding PPG400 and glycerol (Mahmood et al., 2014).

SG) syngas production by lignin gasification and gas cleaning processes. An equivalent ratio equal to 0.2 (pure oxygen/daf lignin) is used in the gasification reactor to obtain the raw syngas (Pinto et al., 2015). For the syngas cleaning, a cyclone, dolomite reactor and scrubber are used to remove dust and tar. An upgrading section is necessary to separate also methane and other volatile compounds (HnCn). Finally, a clean syngas (CO_2, CO, H_2) is obtained for the production of electricity.

3. Optimization methodology and case study

The optimization problem consisted of finding the flowsheet for a lignin-based biorefinery, optimizing an objective function. An economic objective function, Z, was derived as the maximum dry lignin cost the plant can obtain a positive profit:

$$Max\ Z = c_L \tag{1}$$

Where c_L is the supply cost of the dry lignin. A higher supply lignin cost corresponds to a higher net profit. To set the economic analysis, the following constraints were considered:

$$NPV = \sum_{i=0}^{t_{ls}} \frac{CF_i}{(1+r)^i} = 0 \tag{2}$$

Where *NPV* is the Net Present Value, t_{ls} is the life span time for the new plant (20 years plus 3 years for the plant construction), CF_i is the Cash Flow for the year *i*, *r* is the discount rate (considered equal to 3 %). For the calculation of the CF_i, the following equation was considered:

$$CF_i = -f_i TIC + g_i WC + \left(Rev_i + TAC_i + F_{L,i} c_L\right)(1-t) + DPt \tag{3}$$

Where f_i is the fraction of *TIC* spent during year *i* (1/3), describing the investment distribution over the years, *WC* is the working capital (2 % of *TIC*), Rev_i is the annual revenues selling the products, TAC_i is the Total Annual Cost without considering the lignin cost c_L, $F_{L,i}$ is the annual feedstock of dry lignin for the year *i*, *t* is the tax rate (40 %) and *DP* is the depreciation, g_i is a parameter equal to -1 for *i* = 3 (the year before the plant start-up), 1 for $i=t_{ls}$,0 for all other values of *i*. In particular, a straight-line depreciation for ten years was assumed. The optimization problem included the mass and energy balance equations on the units of the superstructure using the product yield of each unit from literature. The number of catalysts, auxiliaries, reactants and the utility flows were estimated by linear relationships with the mainstream flow rates or energy. Equipment costs were estimated by power-law equations with scaling factors. Once the mathematical problem was formulated, a Mixed Integer Non-Linear Problem (MINLP) was obtained. The search for the optimal solution of a MINLP problem might be arduous. As a result, a variable discretization method was applied to linearize the problem (Scott et al., 2013). In particular, for the non-linear relationship for the capital cost, a vector of possible values of the variable was considered (Giuliano et al., 2016). The original variable was set equal to the sum of the product of each of these values and a binary variable. In the problem solution, only one of these binary variables was allowed to be equal to 1. This transformation can be expressed in mathematical terms as follows:

$$\begin{cases} Max\ Z = \alpha x^L + \beta y + \gamma y^d \\ Ax^L + By + Ey^d + \delta = 0 \\ \Gamma x^L + \Delta y + Hy^d + \varepsilon \le 0 \\ x^L \in R^+; y, y^d \in \{0,1\} \end{cases} \tag{4}$$

Where α, β, γ, δ, ε are vectors of coefficients, A, B, Γ, Δ, E, H are matrices of coefficients. In this way, it's possible obtaining a mixed linear problem (MILP) as an approximation of the initial MINLP problem. On the one hand, this simplification allowed using more efficient solution methods for MILP optimization problems. On the other hand, a significant increase in the number of binary variables and real variables was implied. After the complete and linearized superstructure model was obtained, the lignin purchase cost was maximized. In the base case study, a biorefinery fed with 100,000 t_{DRY}/y was considered. Subsequently, a sensitivity analysis varying the size was carried out. In addition to the plant size, the sales prices of the 4 products were also varied to identify the parameter that causes the most extensive variations in the base case to be obtained, including the size, selling price of JF, PFR, PUF, SG. For each parameter, a process optimization was performed to obtain the maximum c_L. In particular, each parameter has been increased to 300 % or decreased to 33 %. Table 1 shows the values of the parameters that have been used to obtain the optimization of the case study for the base case and the values increased or decreased. Furthermore, two different types of lignin were alternatively evaluated in the analysis. The first one is the most widespread in the world, Kraft lignin,

obtained from the processing of paper mills (Humpert et al., 2016). The second one is that obtained after the Organosolv pretreatment process of lignocellulosic biomass, which has been developed in recent years and is widespread in the case of pure and separate lignin production in the first biomass pretreatment step (da Silva et al., 2017).

Table 1: Input parameter values used in the sensitivity analysis

Input parameter	Base case value	Low value	High value
Lignin flowrate (t_{DRY}/y)	100,000	33,333	300,000
JF selling price (€/kg)	0.70	0.23	2.10
PFR selling price (€/kg)	0.80	0.27	2.40
PUF selling price (€/kg)	1.10	0.37	3.30
SG selling price (€/kg)	0.45	0.15	1.35

4. Results

The base case optimization problem was solved for a 100,000 t_{DRY}/y lignin flowrate and selling prices of the products listed in Table 1. The maximum lignin cost obtained through the simulations making feasible the production of PFR was in the range 546-537 €/t_{DRY} independently on the specific process. These values are much higher than the cost of lignin reported in the literature of approximately 51 €/t_{DRY} (Shen et al., 2018). Independently on the lignin origin; therefore, the production of PFR is convenient from an economic point of view, making it the most likely near term application of lignin. Investment costs are around 11 M€ and operating costs around 100 M €/y, mainly due to the reagents for the formulation of the resins (e.g., formaldehyde). Revenues amounted to 155 M€. A sensitivity analysis was performed on the effect of the plant size and products price by varying the base case values by 300 % and 33 %. Corresponding output is reported in Table 1. The optimal values of the lignin cost are reported as bars in the Tornado diagrams of Figure 2 for the case of Kraft lignin as feedstock and of Figure 3 for the case of Organosolv lignin as feedstock. The tornado diagrams report the sensitivity analysis effect as the difference between c_L for the base case and c_L obtained increasing (300 %) or decreasing (33 %) the parameter value (on the horizontal axis). The first parameter on the vertical axis is the parameter with a higher impact on the objective function (higher Δc_L). The last one is the parameter with the lowest impact on the objective function. In Figure 2 and Figure 3, on the left side, the optimal products are decreasing the correspondent parameter to 33 % of the base case value.

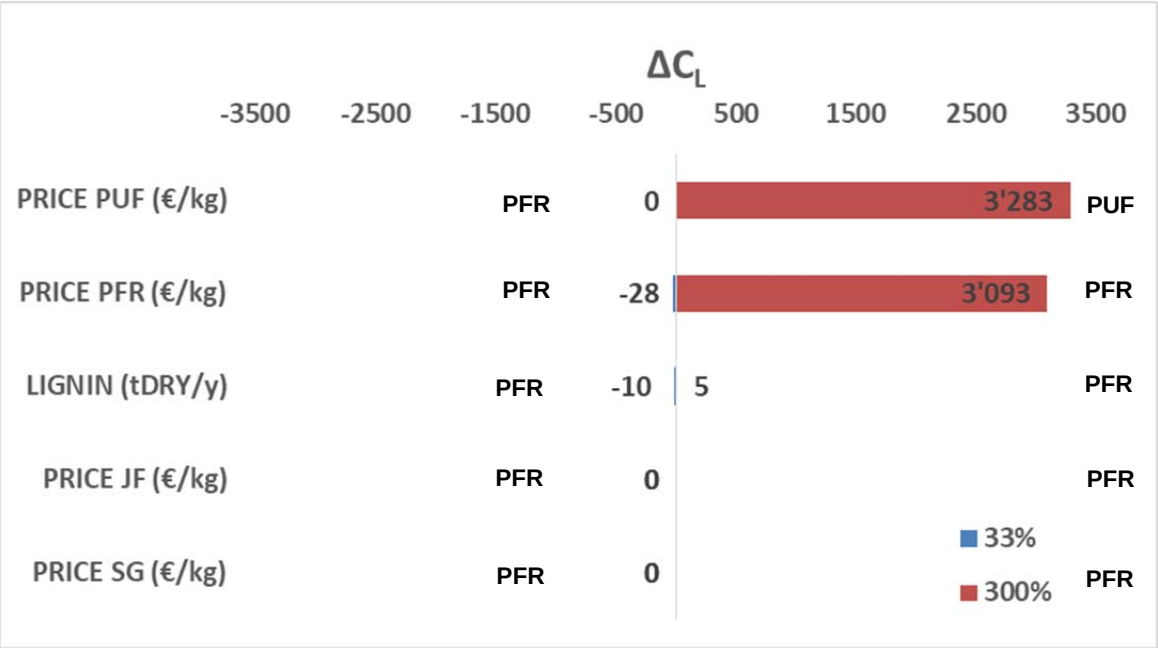

Figure 2: Kraft lignin case. Tornado diagram of the difference between parameter values of 300 % (blue bar) or 33 % (red bar) of the base case and maximum lignin cost for the base case

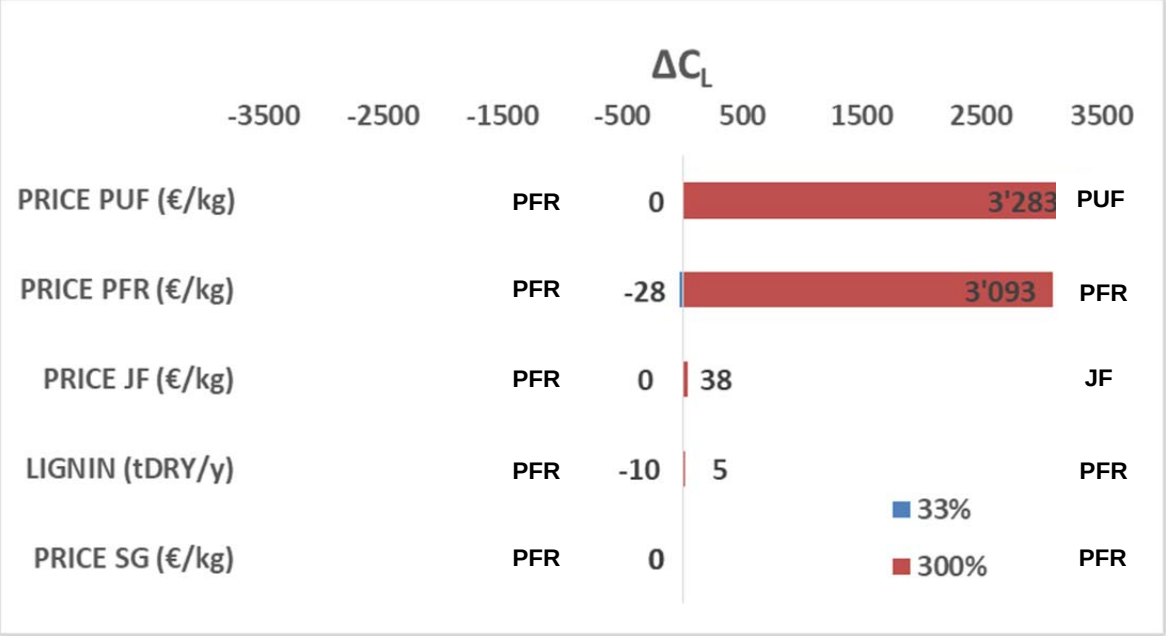

Figure 3: Organosolv lignin case. Tornado diagram of the difference between parameter values of 300 % (blue bar) or 33 % (red bar) of the base case and maximum lignin cost for the base case

On the right side, the optimal products are increasing the correspondent parameter to 300 % of the base case value. The base case results (Δc_L = 0) are reported along the vertical line. The analysis of the diagrams reveals that the prices of PUF or PFR have a significant effect on the maximum lignin cost. In fact, from 546 and 537 €/t_{DRY} for the base case, c_L reached 3,829 €/t_{DRY} and 3,820 €/t_{DRY} for Kraft lignin and Organosolv lignin respectively for the PUF production. In this analysis, Organosolv lignin leads to a maximum lignin cost lower than Kraft lignin utilization producing PFR or PUF. This result derives from lower process yields. In the case of Kraft lignin, the optimal product is always PFR except in the case of a 300 % PUF price for which the optimal product is PUF. In this case (300 % PUF price), TIC was around 28 M€, higher than in the case of PFR production. Also, the TAC was higher, equal to 112 M€/y due to the high cost of glycerol and PPG400. In the case of the use of Organosolv lignin, the price of JF also has a substantial impact on the c_L. In the case of 300 % of the JF base case price, the optimal process was P1 with the production of JF and c_L equal to 375 €/t_{DRY}. In this last case of optimization (300 % JF price), the TIC was around 82 M€, much higher than in the case of PFR production. The TAC, on the other hand, is much lower, at 3.4 M€/y. This result is obtained due to the high investment costs for the pyrolysis sections and hydrodeoxygenation (Vural Gursel et al., 2019). Using a purchase price of pure hydrogen of 2 €/kg (Giuliano et al., 2018), instead, the costs related to reagents in the PUF production process are lower than those for purchasing formaldehyde, wheat flour and alder bark modal of the PFR production process. The lignin cost obtained for the cases of products obtained directly from lignin (PFR andPUF) is higher than the others. This fact is consistent with the bio-based compounds, which avoid the use of fossil fuels, having a better environmental impact (CO_{2eq} savings) (da Silva et al., 2019). For this reason, there are economic benefits (green incentives) for those who produce biofuels (e.g., bioethanol, biodiesel, etc.).

5. Conclusions

This work consisted of the evaluation of technical-economic process analysis of a lignin-based biorefinery. Two different types of lignins (Kraft lignin and Organosolv lignin) were evaluated, and a sensitivity analysis was conducted on five technical-economic parameters, namely plant size, selling price of jet-fuels, of phenol-formaldehyde resins, of polyurethane foams, of syngas for the production of electricity. The most feasible production process resulted in the production of phenol-formaldehyde resins. In the case of the polyurethane foams selling price at 300 % of the base case, the production of polyurethane foams is the only one that maximizes the economic exploitation of lignin. In the case of the selling price of jet-fuels at 300 % of the base case, the production of jet-fuels is the optimal one. The methodology developed in the present work is a valuable tool to analyze and quantify the gap relevant to the selected potential market application of lignin. However, the study still has some limitations since it considers lignin deriving from different biomass.

Furthermore, the data are referred to as non-homogeneous process scales and maturity, and this could affect the mass balance and specific consumption. Further work is needed to more thoroughly assess the feasibility of the processes described in this work considering, for instance, more types of lignins to identify the best conversion process for each type of different raw material.

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