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Techno-Economic Evaluation for Feasibility of Lignin Valorisation Process for the Production of Bio-Based Chemicals

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To reduce the reliance on fossil fuels, alternative energy sources, such as lignocellulosic biomass and agricultural residues, are urgently sought to be recovered and processed to obtain biofuels, chemicals and other high value-added products using diverse processing technologies. In this study, the exergetic and economic evaluation of a lignin valorisation process for catechol production was carried out in order to determine its feasibility. The process is divided into 3 parts: (1) delignification of the feedstock; (2) lignin depolymerisation; (3) products separation.
The investment and operating costs of the process and the obtained catechol market price were estimated. The results showed that the total capital investment of the plant was, approximately, 4.9 M$ based on the plant capacity of 2,544 kg/d of feedstock. Besides, the catechol price was estimated to be 1,100 $/t and the valorisation ratio was found to be 3.02. The obtained results indicate the interesting position of the mentioned product in the market.

1. Introduction

Sustainable economic growth requires suitable raw materials resources for industrial production (Wan et al., 2016). Lignocellulosic biomass is being increasingly considered as a sustainable and low-cost feedstock for the production of fuels, energy and commodity chemicals, under the intense fractionation scheme of a biorefinery (Yu et al., 2017). In the biomass processing technology, some of the most significant parameters are the capital cost of the plant, the energy demand, the type and cost of raw material and its suitability for biobased chemicals production. A considerable amount of published papers can be found related to the technical design, process simulation and economic assessment of lignocellulosic biomass processing technologies. Sassner et al. (2008) investigated a techno-economic evaluation of a biorefinery for the production of bioethanol from three different lignocellulosic materials (salix, corn stover and spruce). Laure et al. (2014) analyzed the economic feasibility of a biorefinery process based on an organosolv pre-treatment which converted wood into glucose, lignin and xylose rich streams.
Moreover, several integrated biorefinery schemes have been submitted to economic studies. Misailidis et al. (2009), evaluated the feasibility of commercial arabinoxylan production in the context of a wheat biorefinery principally producing ethanol. Moncada et al. (2013) presented a techno-economic analysis for a sugarcane biorefinery based on two scenarios for different conversion pathways as function of feedstock distribution and technologies for sugar, fuel ethanol, PHB, anthocyanins and electricity production. Sadhukhan and Ng (2011), studied the process modelling and integration of biorefinery and chemical processes based on the whole system life cycle analysis tools. In this context, the aim of this work was to investigate the economic viability of the lignin valorisation process using lignocellulosic biomass for catechol production. The evaluation was performed adopting the economic analysis methodology presented by Wan et al. (2016). Moreover, an exergetic assessment (physical exergy calculation) of the underlying process is presented.

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2. Process description

The simulation of the studied process was performed by Aspen Plus®. The process can be divided into three main sections: biomass fractionation, lignin depolymerisation and products separation stages.

2.1 Biomass fractionation stage

The olive tree pruning used as feedstock in the studied process was treated with ethanol water in the biomass fractionation stage of the process.

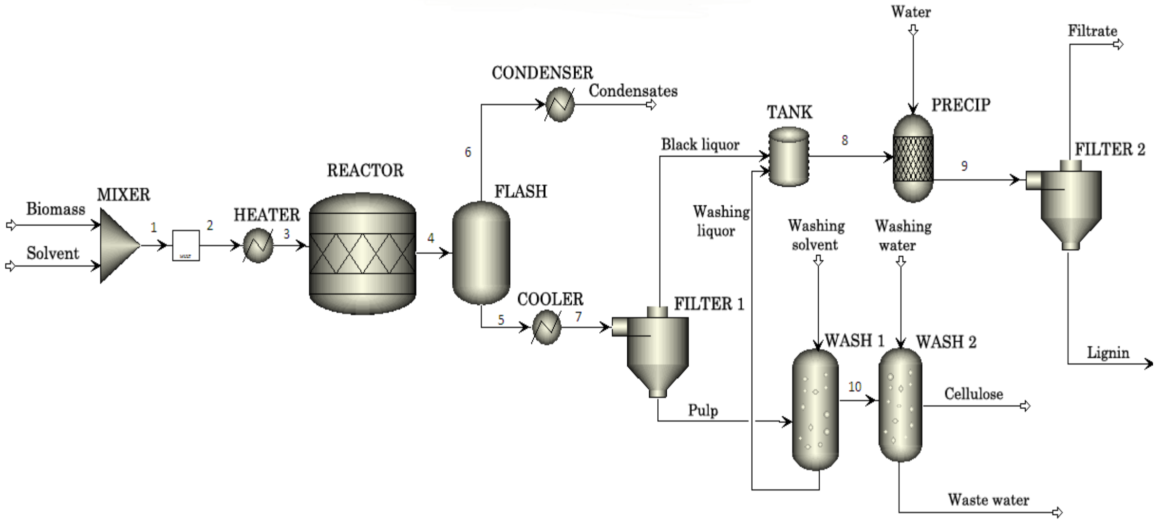

Figure 1: Biomass fractionation stage

Five main sections can be distinguished (Figure 1): (1) the delignification section, where the lignocellulosic biomass is fractionated with ethanol under well-defined operating conditions (1 kg/h of dry raw material was mixed with 6 kg/h of ethanol –water solution with a concentration of 1:7 in weight, and fed up to the reactor which worked at 200 °C); (2) the separation section of the slurry; (3) the cellulosic solid fraction processing (washing); (4) the filtration section and (5) the precipitation of lignin (Mabrouk et al., 2016).

2.2 Lignin depolymerisation stage

The solid lignin obtained and separated from the fractionation of the olive tree pruning was depolymerised under an alkaline treatment. The lignin was mixed and dissolved with a solution of sodium hydroxide (4 wt. % of NaOH) in a solid to liquid ratio of 1:20 in weight. Afterwards, the solution was heated and introduced to the depolymerisation reactor (300 ºC, saturated liquid).

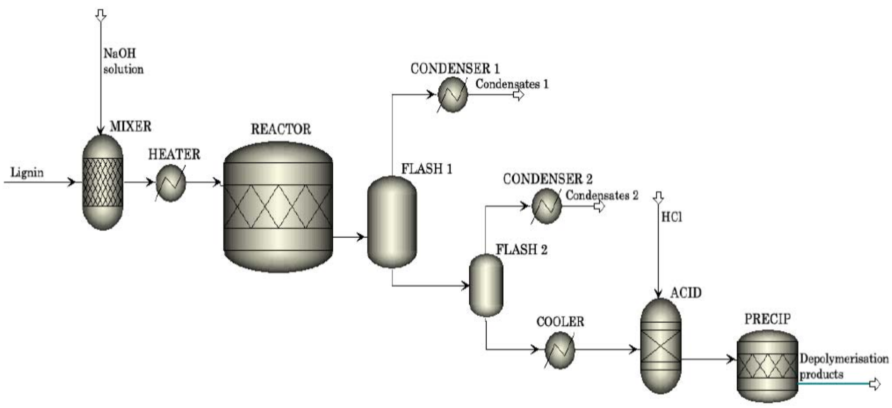

Figure 2: Lignin depolymerisation stage

The resulting slurry was then expanded in two consecutive flash units, obtaining two vapor streams mainly composed of water and some volatile compounds, and cooled. Hydrochloric acid was added in order to precipitate the tar (residual lignin + char) formed in the reaction. Figure 2 presents the flowsheet of the lignin depolymerisation stage.

2.3. Products separation stage

The main objective of this part was to isolate the catechol and the oil from the rest of the products. Catechol is the target product in the proposed lignin revalorization route. All the resulting products and sub-products were separated in successive units of the third stage, as presented in Figure 3.

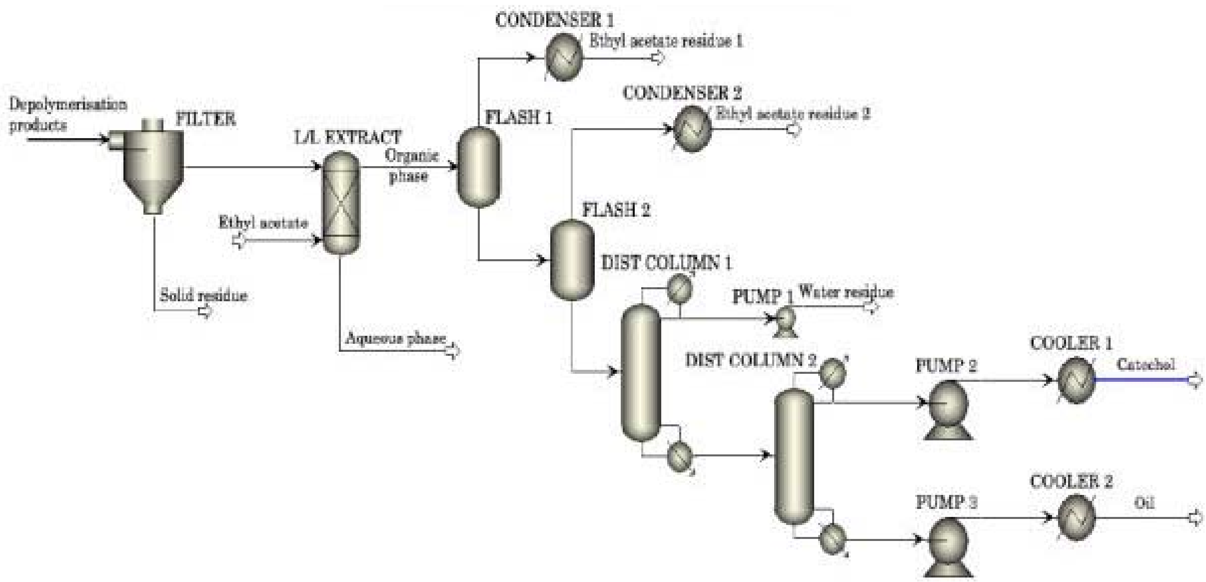

Figure 3: Products separation stage

Firstly, the tar was separated from the liquid slurry by filtration in the unit named FILTER. All the tar was retained in the filter and the liquid slurry was subjected to a liquid-liquid extraction in the unit named L/L EXTRACT. Afterwards, the organic phase was introduced in two steps of flash tanks under vacuum atmosphere. Almost all the ethyl acetate was recovered in this step and part of the water was removed as well. In order to remove the rest of the water, a distillation column (DIST COLUMN 1) was added. Finally, the catechol was separated from the phenolic oil composed by other monomers and oligomers by another distillation column (DIST COLUMN 2).

3. Exergy and economic assessment

The exergy balance for a flow process in a system during a finite interval may be written by Eq(1):

Exergy input – exergy output – exergy consumption = exergy accumulation (1)

The total revenue requirement (TRR) method (Bejan et al., 1996) was applied to perform the economic analysis of our process. This approach is divided in three steps: estimation of the total capital investment; calculation of the total revenue requirement and the calculation of the levelized cost, which is given by Eq(2) and (3).

$$A = CRF \sum_{m=1}^{n} P_m \tag{2}$$

$$CRF = \frac{i \times (1+i)^n}{(1+i)^n - 1}; \quad P_m = C_m \left(\frac{1}{(i+1)^m} \right) \tag{3}$$

where **i** is the interest rate on capital and n is the period of payment (number of annuities). Following the mass balances, the valorization ratio for each pretreatment method can be assessed. This ratio is determined by Eq(4) (Albarelli et al., 2016).

$$\% \ valorization \ ratio = \frac{Value \text{ of output product (\$/kg)}}{Cost \ of \text{ feedstock (\$/kg)}} \quad (4)$$

The capital and operating costs were estimated using the software Aspen Economic Analyzer®. Some specific parameters regarding to Spanish conditions, such as the raw material costs, annual interest rate and labor salaries, among others, were identified in order to calculate the production costs per unit for the target product. This analysis was estimated in USD for a 15-y period. All these parameters are updated to the reference year 2016. The capital depreciation was calculated using the straight-line method. The list of the assumptions and data used in this analysis can be found in Tables 1 and 2.

Table 1. General assumptions for the studied process

Economic parameter	Value
Interest ratio *(i)*	5%
Plant economic life *(n)*	15 y
Number of working hours per year (τ)	8,760 h
Electricity	5,96 $/h
Utilities	0.53 $/h
Capital recovery factor *(CRF)*	0.159

Table 2. Cost of chemical products for the studied process

Chemical product	Cost ($/kg)
Ethanol (C_2H_5OH)	0.55
Hydrochloric acid (HCl)	0.2
Sodium hydroxide (NaOH)	0.35
Ethyl acetate ($C_4H_8O_2$)	0.96

3. Results and discussion

3.1 Process exergy balance

For the whole biorefinery process considered in this study, exergy balance calculations were performed for the abovementioned stages. The exergy balance is described in Eq(5), where the difference that results in balancing of all entering and leaving exergy flows is denoted as exergy loss.

$$\sum(1-\frac{T_0}{T})Q - W + (\sum_i m_i Ex_i)_{in} - (\sum_i m_i Ex_i)_{out} = Ex_{destruction} = T_0 S_{generation} = I \quad (5)$$

The exergy losses were found to be around 222 kW. The biomass delignification stage was responsible for the most part of the exergy losses. In fact, it contributed with a 44 %, whereas the lignin depolymerisation stage was responsible of a 34.5 % and the products separation part of a 21.3 % as it is shown in Figure 4. The exergy losses would be probably associated to the temperature of the mentioned stages.

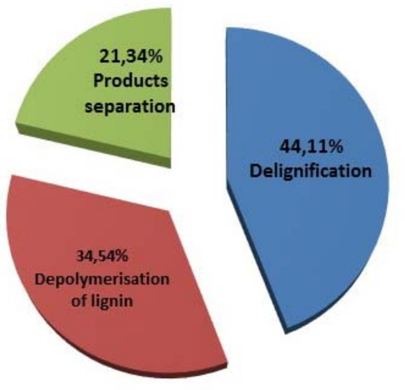

Figure 4: Exergy losses contribution per stage

3.2. Economic analysis

For the estimation of the total capital investment (TCI), the fixed-capital investment should be approached. For this purpose, the purchased-equipment costs (PEC) were determined by Aspen Economic Analyzer®. Table 3 shows a division into categories of the TCI.

Table 3. Total capital investment and related cost

Designation	Cost (M$)
Purchased Equipment cost (PEC)	0.76
Purchased equipment installation	0.42
Piping	0.50
Instrumentation and control	0.15
Electrical Equipment and material	0.08
Onsite cost (ONSC)	1.91
Land	0.04
Civil, structural and architectural work	0.16
Service facilities	0.49
Off cost (OFSC)	0.69
Fixed capital investment (FCI)	3.71
Start-up cost	0.22
Working Capital (WC)	0.11
Allowance for funds used during construction (AFUDC)	0.82

The ratio factors related to (PEC) were selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of ± 30 % (Sadukhan et al, 2014). Figure 5 presents the total purchased equipment costs per each stage.

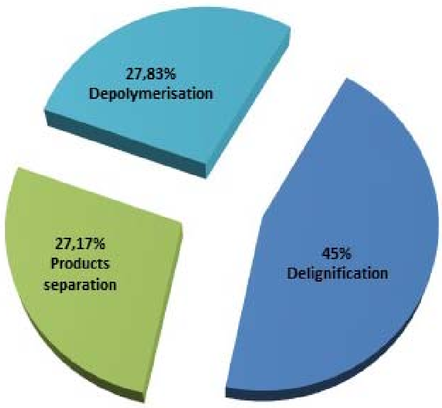

Figure 5: Total purchased equipment costs (PEC) per stages

According to Figure 5, the biomass fractionation stage was found to be the most expensive part, representing the 45 % of the total purchased equipment cost (PEC). The availability of the raw material, the quality and the price of the lignocellulosic biomass used in the lignin recovery process are key factors in the profitability of a biorefinery project (Ghezzaz, 2011). The estimated total investment cost (TCI) of the process thus calculated is, approximately, $4.87 \cdot 10^6$ $. This cost is relatively low compared to the investment cost of similar processes published in the literature. This fact is mainly due to the lower production capacity of the studied process, which is of 4,700 kg lignin/y. Lee et al. (2011) published a total capital investment for biodiesel production processes at the capacity of 40,000 t/y between 11.1 and 15.6 10^6 $ and a total manufacturing cost, for the same processes, between $29 \cdot 10^6$ and $46 \cdot 10^6$ $. Kautto et al. (2014) presented an organosolv process with a hardwood feed of 2,350 t/d and a total capital investment of approx. $720 \cdot 10^6$ $. The levelized total requirement revenue (TRRL), the levelized operation and maintenance cost (OAML) and the levelized fuel cost (FCL) were calculated and are summarized in Table 4.

This way, the levelized carrying charges (CCL) and the levelized catechol market price were determined. It was found to be 1,100 $/kg, similar to the cost published in the literature (Lavoie, 2011). It is important to mention that there are uncertainties regarding the cost of the different raw materials, as well as the process itself, with its equipment cost. The valorisation ratio in this study was found to be 3.02.

Table 4. Levelized cost of the studied plant

Levelized cost	**Value** ($)
The levelized total required revenue (*TRR_L*)	15.95
The levelized fuel cost (*FC_L*)	0.12
The levelized operation and maintenance cost (*OAM_L*)	14.31
Carrying Charges (*CC_L*)	1.51

4. Conclusions

In this study, a techno-economic evaluation of a lignin valorisation process for the production of bio-based chemicals was investigated. The obtained results showed that the total capital investment of the plant was approximately estimated to be $4.87 \cdot 10^6$ \$ based on the plant capacity of 2,544 kg feedstock/d. The catechol price was estimated to be 1,100 $/t and the valorisation ratio was found to be 3.02. The obtained result strongly depended on the assumptions of the price for raw material and the market prices for the products. Sensitivity analysis should be conducted to further investigate this research helping to understand the most significant parameters from an economic perspective.

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