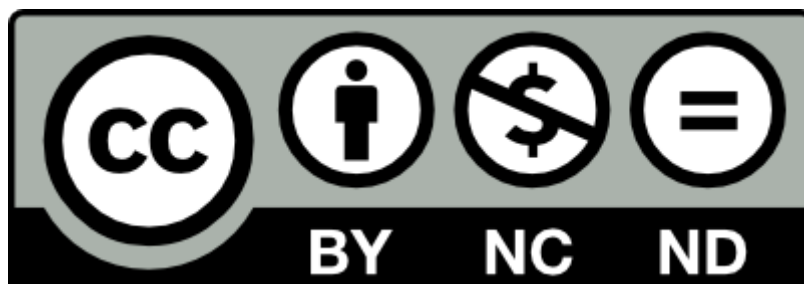


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Abstract: Recently, the valorization of the lignin fraction in the biorefinery scheme is getting more and more attention as the use of this component for the production of bio-based chemicals is crucial for the success of the integral development of lignocellulosic biorefinery processes. The present work includes the exergy performance and the economic analysis of a process for catechols production using lignin extracted from olive tree pruning. Energy and exergy calculations were obtained from the process simulation with Aspen Plus®. The exergy analysis was applied to identify the units associated with the main irreversibilities and exergy losses. The process investment and operating costs were determined as well as the derived catechol market price. The calculated total plant capital investment was about 4.9 M\$ for a plant capacity of 2544 kg feedstock/day. The estimated catechol price was 1100 \$/t with a valorization ratio of 3.02. These results place the product in a competitive position in the market.

Keywords: Lignin, Valorization, Catechol, Economic analysis, Energy and exergy balances, Aspen Plus®



Economic analysis of a biorefinery process for catechol production from lignin

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ABSTRACT

Recently, the valorisation of the lignin fraction in the biorefinery scheme is getting more and more attention as the use of this component for the production of bio-based chemicals is crucial for the success of the integral development of lignocellulosic biorefinery processes. The present work includes the exergetic performance and the economic analysis of a process for catechols production using lignin extracted from olive tree pruning. Energy and exergy calculations were obtained from the process simulation with Aspen Plus[®]. The exergetic analysis was applied to identify the units associated with the main irreversibilities and exergy losses. The process investment and operating costs were determined as well as the derived catechol market price. The calculated total plant capital investment was about 4.9 M\$ for a plant capacity of 2,544 kg feedstock /day. The estimated catechol price was 1100 \$/t with a valorization ratio of 3.02. These results place the product in a competitive position in the market.

Keywords: Lignin, valorisation, catechol, economic analysis, energy and exergy balances, Aspen Plus[®].

INTRODUCTION

The bio-based industry is being promoted as an interesting option for energy, materials and chemicals production as an alternative to fossil resources (Parada et al, 2017). Environmental concerns have raised the attractiveness of biomass based renewable raw materials as well. Good performance in environmental and social terms is attributed to the integral biorefinery technology which uses non-food biomass resources, such as lignocellulosic biomass, for the production of high value co-products (Bennett, and Pearson, 2009).

Indeed, bio-based industry is a pillar of European Union Horizon 2020 program for sustainable development (Puigjaner et al., 2015). Lignocellulosic biomass is available all over the world, abundant, renewable, cheap and does not enter in competition with food industry (Schmetz et al., 2016). In this context, the petroleum-based chemical industry needs to perform a progressive shift towards a bio-based chemical economy. In fact, it has been estimated that lignocellulosic biochemicals could represent sales of about \$ 600 billion by 2025 (Kokossis et al., 2015) and that the associated bio-based industry could require up to 90,000 work positions by 2030 (Sadhukhan et al., 2016). An integrated biorefinery scheme should make use of all the parts of the lignocellulosic biomass, namely cellulose, hemicelluloses and lignin (Mahmoud et al., 2016). The core concept of a biorefinery is based on biomass conversion technologies into hydrocarbon fuels and chemicals in the same way that the petrochemistry industry does (Biddu et al., 2016). Biorenewable chemicals structures and functionality can provide the wide range of products that are currently obtained from petrochemistry (Gunukula et al., 2016). Lignocellulosic biomass bioproducts are directly dependent on the used feedstock and fractionation technology. The competitiveness of the generated chemicals relies on the use of an efficient use of the raw material, reactants and solvents (Alexandri et al., 2016). The valorization of lignin is decisive in the integrated biorefinery concept (Azadi et al., 2013). The phenolic-rich chemical structure of this polymer, mainly formed by methoxylated phenylpropane structures, is a source for the production of formulations based on bio-phenols or bio-polyols such as resins (Wang et al., 2009). In fact, lignin represents the most abundant bio-based source of aromatics structures available. Several aromatic polyols, such as cresols, catechols or resorsinols, that preserves the lignin monomer structure, can be obtained by different techniques such as catalytic depolymerization (Zhang et al., 2014), hydrodeoxygenation (Liu et al., 2016), thermal treatments, catalytic hydrogenation, hydrocracking, oxidation or hydrolysis (Zakzeski et al., 2010). The obtaining of high quality lignin streams, in terms of purity and low polydispersity, is the first step in the production of these derivatives from lignin (Mahmoud et al., 2016) and they can be obtained from the fractionation of lignocellulosic biomass by methods as organosolv processes (González Alriols et al., 2010) or the LignoBoost technology (Zakzeski et al., 2010). The advantages of organosolv lignin respect to Kraft and sulphonated lignins include the absence of sulphur, more ability to be derivatised, lower inorganics content, higher purity and lower hydrophobicity. This characteristic makes organosolv lignin suitable for the obtaining of value added chemicals (Mahmoud et al., 2016). The above mentioned compounds are closely related to the basic building blocks of lignin and their production at large-scale scale could be highly desirable. Nevertheless, markets and applications for monomeric lignin building blocks need further development and several challenges related to the heterogeneous composition of lignin compounds should be overcome (Werpy and Petersen, 2007). Indeed, the integration of a

lignin process stream within the biorefinery requires to carefully define the best way to cost-effectively separate the lignin stream from the original biomass source considering the particular characteristics of this component, as its structural variability, reactivity and thermal stability (Werpy and Petersen, 2007). Two important goals must be defined for the achievement of a proper techno-economic performance of biorefinery processes. One is related to the defining of primary cost drivers and the other one relies on the risks associated to industrial scale-up (Bidy et al., 2016). It is, therefore, worthwhile to investigate the technoeconomic aspects of converting lignin into value-added products (Azadi et al., 2013), including biofuels (Obydenkova et al., 2017). For the latter point, it is compulsory to locate the process bottlenecks, to optimize the production yield and minimize capital expenditures (Gargalo et al., 2016). Studies related to the techno-economic assessment of lignocellulosic biorefineries can be found in the literature, based on the use of biomass wastes, such as citrus residues (Lohrasbi et al., 2010) or corn stover (Luo et al., 2010) and wood (Laure et al., 2014). Some studies have focused in the techno-economic assessment of selected bio-based chemicals. Some examples include the lactic acid obtaining process (Sikder et al., 2012), the obtaining of bio-based products derived from glutamic acid (Lammens et al., 2012), the production of bio-based succinic acid from carbohydrates (Cok et al., 2014), the valerolactone obtaining from lactic acid and its esters (Tang et al., 2014) and the n-butanol production from sugarcane sugars (Pinto Mariano et al., 2013). Another key point for the process sustainability is the energy efficiency, as this factor is always closely related to the process environmental and economic performance. A widely accepted criteria for the evaluation of the energy efficiency is the exergy analysis, based on the second law of thermodynamics, as it provides an interesting way of assessing yield efficiencies indicating how closely actual performance approaches the ideal. It works by identifying the origin, locating energy degradation within a process (Ojeda et al., 2011) and allowing the introduction of improved and optimized designs (Mabrouk et al., 2016a). By considering both energy and exergy efficiencies, the quality and quantity of the energy required in a process can be estimated and, thus, the energy efficiency improved, allowing the compliance of energy policy objectives (Kanoglu et al., 2008). Studies of the exergetic performance of several biorefinery processes can be found in the literature, as the ethanol production process from lignocellulosic biomass (Ojeda et al., 2011) or the combined ethanol and biogas generation technology (Bösch et al., 2012). Nevertheless, few examples of complete exergy analyses applied to biochemical pathways can be found in bibliography, such as the work by Ojeda et al. (2009), in which a lignocellulosic biomass enzymatic hydrolysis process for the production of second generation bioethanol fuels was analyzed in terms of exergetic performance using ASPEN-HYSYS®. Tan et al. (2010) presented the analysis of the production process of second-generation bio-ethanol. A similar study was applied to the bioethanol obtaining process from straw (Modaresi et al., 2011).

Residual biomass was used as feedstock as well by Velásquez Arredondo et al. (2009). Lythcke-Jørgensen et al. (2013) studied, in terms of exergy performance, the integrated production of heat, power and lignocellulosic ethanol in a poly-generation system based on an existing Combined Heat and Power unit and concluded that it was very interesting and innovative to analyze the exergy of the integrated process, as these types of analysis had been typically performed for thermochemical pathways or to biofuel production processes and very few studies presented the results applied to combined thermochemical and biochemical pathways.

This contribution focuses on the exergetic and economic analyses of process for phenolic compounds obtaining, particularly catechols, from the lignin fraction obtained by fractionation of lignocellulosic biomass (olive tree pruning). The study was based on a model developed with Aspen Plus[®] software using laboratory experimental results. The economic analysis followed the methodology presented by Sadhukhan et al. (2014). In fact, thanks to its wide array of applications in pesticide and pharmaceutical fields, catechol has been chosen as the target product in this study from lignin revalorization route proposed. The current market price for catechol is close to 2000 USD/t that makes it so interesting from the economic point of view. Hence, this work is the first contribution focusing on the exergetic and economic analyses of process for catechols obtaining, from the lignin fraction obtained by the fractionation of lignocellulosic biomass (olive tree pruning).

2. MATERIALS AND METHODS

2.1 Process description

Olive tree pruning (Arróniz variety from Ayegui, Navarra, Spain) has been the feedstock used in this study. The results of the chemical characterization (Mabrouk et al., 2016a) revealed a high cellulose content in the raw material, representing more than half its composition. Lignin was the most abundant component after cellulose with a 23% in weight and the hemicelluloses percentage was around 13%. In order to separate each main component of the lignocellulosic biomass structure (cellulose, hemicelluloses and lignin) for its subsequent valorisation, several treatments were developed. The process was divided in three stages: (1) biomass fractionation by organosolv ethanol treatment, (2) lignin depolymerization and (3) products separation. The flowsheets of the three stages, the used operational conditions can be found in a previous work (Mabrouk et al., 2017) as well as the main reactions used to represent the biomass fractionation in the simulation with Aspen Plus[®] (Mabrouk et al., 2016b) . The reactions used

to model the lignin precipitation module included in stage (1) are presented in Table 1. The main reactions used to model stage (2) are presented in Table 2.

The simulation of the precipitation unit of stage (2) was performed in two separate reactors. In the first one, the pH of the solution was reduced to 1 in an RGibbs reactor to calculate the energy produced in the acidification process. The neutralisation reaction occurred was:



Once pH = 1 was reached, the precipitation of the tar was simulated in another reactor. Besides tar, ash and NaCl also precipitated in this step. This mixed stream with the depolymerization products was the feed of stage (3), where the separation of the final products, catechols, was achieved.

2.2 Modelling approach

The design and modelling of the entire process, including its three stages, was done with Aspen Plus[®]. Cellulose, hemicelluloses and lignin were defined, on the one hand, by their chemical structure and physical properties (Wooley and Putsche, 1996) and, on the other hand, by chemical characterisations done in the laboratory. The selected thermodynamical model for the simulation was NRTL-RK (Non-Random, Two Liquids-Redlich-Kwong). However, the liquid-liquid extraction process was simulated with UNIQUAC model, in accordance to Wooley and Putsche (1996).

2.3 Methodology: energy and exergy analysis

The exergy of a system is defined as the maximum useful work that can be obtained from a process by bringing the system into thermodynamic equilibrium with the surroundings through reversible processes (Peters et al., 2015). Exergy, which unlike energy do not follow the law of conservation, represents the energy that is available in the process. Exergy can be destroyed by irreversible processes being this destruction proportional to the entropy increase of the system together with its surroundings. An evaluation of the system behavior based only in material and energy balances is not enough to evaluate the process performance as in energy balances the different forms of energy are not distinguished. By considering both enthalpy and entropy flows under the exergy concept, it is possible to assess the quality of energy (Peters et al., 2015). Very useful information can be extracted from an exergy analysis because, by the identification, location, and measurement of the process thermodynamic inefficiencies, improvement strategies can be proposed in the steps responsible of the highest losses and different process configurations can be defined and compared (Asprion et al., 2011).

Eq. 1 describes the balances, in terms of energy and exergy, for a control volume (Borgnakke and Sonntag, 2012):

$$\sum \dot{Q}_{CV} + \sum \dot{m}_i h_i = \dot{W}_{CV} + \sum \dot{m}_e h_e \quad (1)$$

Exergy losses or irreversibility, I , is the difference between the exergy of the entering and leaving streams (Eq. 2):

$$\sum (1 - \frac{T_0}{T}) \dot{Q} - \dot{W} + (\sum_i \dot{m}_i Ex_i)_{in} - (\sum_i \dot{m}_i Ex_i)_{out} = Ex_{destruction} = T_0 S_{generation} = I \quad (2)$$

The total exergy balance of a process considers the exergy input, output and consumption to define the exergy accumulation (Eq. 3):

$$\text{Exergy input} - \text{Exergy output} - \text{Exergy consumption} = \text{Exergy accumulation} \quad (3)$$

2.4 Economic assessment

After having determined the target product and operational data for this study case, a cost analysis was performed to establish the process economical feasibility. The total revenue requirement (TRR) method (Bejan et al., 1996), which consist of three steps, (1) the estimation of the total capital investment, TCI; (2) the calculation of the total revenue requirement, TRR, and (3) the determination of the levelized cost, LC, was applied in this contribution. The TRR was defined as a varying annual amount and, for its calculation, the operating and maintenance costs, OAM, as well as the fuel costs, FC, variations due to inflation were considered. The financing plan interest rates were calculated as well.

The total revenue requirement for the j^{th} year, TRR_j , that is presented in Equation 4, can be determined by the sum of all annual amounts: the Total Capital Recovery, TCR; the minimum Return On Investment, ROI, the OAM and the FC (Bejan et al.,1996):

$$TRR_j = TCR_j + ROI_{j,ce} + ROI_{j,ps} + ROI_{j,d} + OAM_j + FC_j \quad (4)$$

ROI can be calculated for common equity (subscript ce), preferred stock (subscript ps) and debt (subscript d).

In order to determine the catechols levelized Carrying Charges (CC_L) and levelized Selling Price (SP_L), the levelized Total Required Revenue (TRR_L), the levelized Operation and Maintenance costs (OAM_L), and the levelized Fuel Cost (FC_L) were calculated.

The input information necessary to perform the economic analysis includes the annual values of carrying charges, raw water cost, FC and OAM expenses, which are, all of them variable factors that may vary considerably during the economic life (Atmaca et al.,2014). Thus, an

independent parameter is used for the analysis, the Levelized Annual Value (LAV). The LC is determined by Eq. 5 and 6 (Bejan et al., 1996):

$$A = CRF \sum_{m=1}^n P_m \quad (5)$$

$$CRF = \frac{i \times (1+i)^n}{(1+i)^n - 1} \quad (6)$$

$$P_m = C_m \left(\frac{1}{(1+i)^m} \right) \quad (7)$$

where the following parameters appear: i : interest rate on capital; n : payment period expressed as number of annuities. The valorization ratio, VR, can be determined as is expressed in Eq. (8) (Albarelli et al., 2016).

$$\% \text{ Valorization ratio} = \frac{\text{Value of output product } \left(\frac{\$}{\text{kg}} \right)}{\text{Cost of feedstock } \left(\frac{\$}{\text{kg}} \right)} \quad (8)$$

The estimation of the investment cost depends on the reliability of available data on equipment purchased prices and on the information on the technical specifications corresponding to the equipment industrial processes (Peters et al, 2003).

3. Results

3.1 Energy Analysis

The results related to energy consumption of the main streams of the studied process obtained from the simulation with a calculation basis of 100 kg/h of biomass are displayed in Table 3. For stage (1), the following input streams were defined: biomass, solvent, washing solvent (Wash S), washing water (Wash W) and water. As output streams, condensates, cellulose, waste water (Waste W), filtrate and lignin were defined. Lignin, which is the product of interest, was fed to stage (2). In stage (2), the present input streams were: lignin, sodium hydroxide solution (NaOH) and hydrochloric acid solution (HCl). Regarding the output ones, two of the three streams of this stage correspond to condensate products (Cond 1 and Cond 2) and the third one is formed by depolymerization products (DP), which were fed to stage (3). In this last stage, DP are mixed with ethyl acetate and catechols, oil, solid residue (SR), ethyl acetate residue 1 (EtAc res 1), ethyl acetate residue 2 (EtAc res 2), water residue (Water res) and

aqueous residue (Aq. res) are obtained as output streams. As it can be seen, the amount of obtained oil was 2.57 kg/h. In the oil stream, some catechols were dissolved as it was impossible to separate completely these compounds. Regarding the catechols stream, 0.54 kg/h were obtained.

3.2 Exergy Analysis

The results of the exergy balances of stages (1), (2) and (3) are shown in Table 4, where the exergy losses calculated for the main equipment of each stage of the studied process are indicated in Table 5. The global biorefinery process presented 222 kW of exergy losses from which a 45% was located in stage (1), the biomass delignification stage. A 34% and a 21% were attributed to stages (2) and (3), respectively.

3.2.1 Results of stage (1), biomass fractionation stage

The results of the exergy losses for each equipment of stage (1) are summarized in Figure 1. The total exergy losses attributed to this stage were around 98 kW. A 44% of this quantity was located in the delignification section, in which a 28% of irreversibilities were associated to the heater and a 16% to the reactor. After the reaction, the separation and condensation processes implied a 21% of the total losses, respectively. No more significant contributions to irreversibility were found in stage (1). Thus, as the heater was the equipment with the highest exergy loss in this stage, it was concluded that the generated irreversibility could be associated to the higher heat transfer between input and output streams. The contribution of the reaction process was considerable as well. In this case, the definition of the reaction parameters in the simulation did not include kinetic factors (Mabrouk et al, 2016a).

<Figure 1. Exergy losses contribution of the biomass fractionation stage.>

3.2.2 Results of stage (2), lignin depolymerization stage

The exergy losses per equipment of the depolymerization stage are shown in Figure 2. In this part, the total exergy losses were estimated to be 76.7 kW. Heater 2 was the main responsible for these losses, with a contribution close to 37%. Furthermore, the reactor, Condenser 1, Condenser 2 and the ACID unit contributed respectively with 10.7% ,10.6%, 12.8% and 15.8%.

<Figure 2. Exergy losses Contribution in the lignin depolymerization stage.>

3.2.3 Results of stage (3), products separation stage

The exergy losses for this stage were found to be 47.4 kW. The filter was the main responsible for the irreversibility generated in this unit. It contributed with a 58.8%, whereas Flash 1 and the condenser were responsible of 21.5% and 17% respectively (Figure 3). The contribution of the other equipment was considered negligible.

<Figure 3. Exergy losses contribution in the products separation stage.>

3.3 Economic analysis

3.3.1 Total cost investment (TCI)

The main purpose of the economic evaluation has been to calculate the selling price of catechols by determining the most relevant costs of the process, as the operating variable and fixed expenses, the capital costs, the investment, etc. The equipment purchased price and corresponding sizes were gathered from previous studies (Mabrouk et al., 2017) and some calculations were performed with Aspen Process Economic Analyzer V8.8[®]. The Chemical Engineering Plant Cost Index (CEPCI, 2016) was used for the estimation of the equipment price. The total capital cost, TCC, is the summation of direct costs (equipment, installation, instrumentation-control, piping, electrical systems, building, yard improvements and service facilities) indirect costs and working capital (Sadukhan et al., 2014). To calculate the TCC, it is necessary to determine the purchased-equipment costs (PEC). Table 6 presents the values of PECs for the studied process. The ratio factors for PEC calculations, even if were selected according to the process characteristics, could have uncertainty levels between of 30% - 50% associated to the capital investment calculations due to the complexity level of the analysis (Sadukhan et al, 2014). Other particular data related to local providers, annual interest rate or labor salaries were considered as well for the production costs estimation per unit of the target product. This data was updated to the reference year 2016 and calculated for a 15-y period. The straight-line method was selected for the capital depreciation estimation. The estimation of TCI was done with data from a previous work, as well as other assumptions and data required for the study (Mabrouk et al., 2017). The annual operating and maintenance costs are presented in Table 7. The obtained results indicated that stage (1) was the most expensive unit representing the 45% of the total PEC, followed by depolymerization and products separation units, which contributed with a 27.5% each. The estimated process TCI was, approximately, 4.87 million \$, which is quite low if we compare it with other TCI values

published for similar processes (Kautto et al., 2014). This fact can be attributed to the low production capacity of the studied process of about 4700 kg of lignin / year.

3.3.2 Calculation of the Total Revenue Requirement (TRR)

The calculated value of the Total Revenue Requirement was found to be $TRR = \$ 100M$. In this section, the TRR_L , the OAM_L and the FC_L were calculated and are presented in Table 8. These results are necessary to perform a thermoeconomic analysis, which differs from a conventional economic analysis in the fact that the former is done at the plant component level. For the calculation of the levelized costs, the capital recovery factor as well as the economical concept of levelization have to be introduced. The CC_L and the levelized selling price of catechols were estimated. The latter, defined as the main-product unit cost and was found equal to 1100 \$/kg. This value is in concordant with the cost published in the literature (Lavoie, 2011). Moreover, the valorization ratio in this study was calculated to be 3.02.

4. Conclusions

In this study, a brief technico-economic assessment was made as a first evaluation of the economics of a lignin processing scheme for bio-based products obtaining, particularly, catechols. Firstly, the exergy performance of the studied process was investigated and, then, an economic evaluation was carried out. The total irreversibility was estimated to be 222 kW of which, approximately 44% was located at the biomass fractionation stage. The economic results offered a plant TCI of about 4.9 M\$ based on a plant capacity of 2544 kg of feedstock per day and a catechols price of 1100\$/t with a valorization ratio of 3.02. The result, even if strongly dependent on the raw materials' price assumptions and on the selling prices for the products, gives an idea of the position of this bio-based product in the market.

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Figure captions

Figure 1. Exergy losses contribution of stage (1), the biomass fractionation stage.

Figure 2. Exergy losses contribution of stage (2), the lignin depolymerization stage.

Figure 3. Exergy losses contribution of stage (3), the products separation stage.

Figure 1.

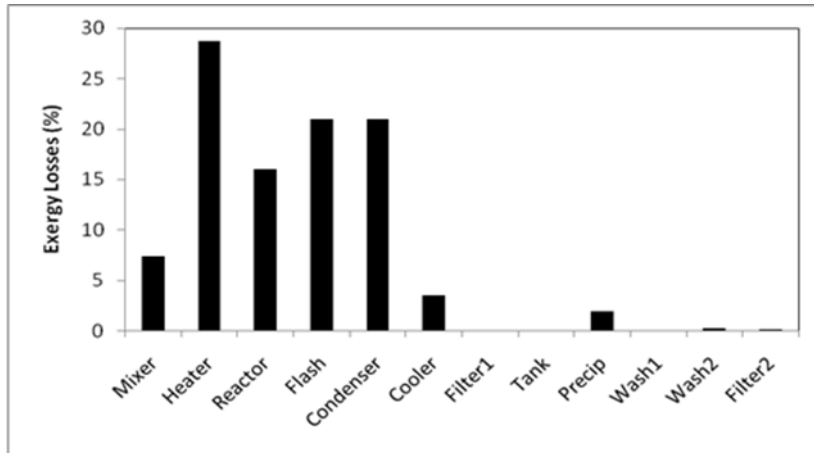


Figure 2.

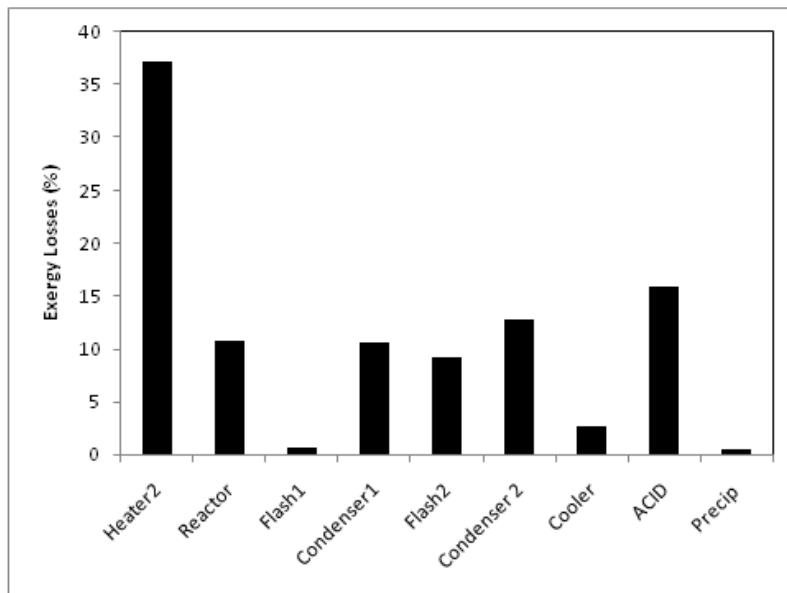


Figure 3.

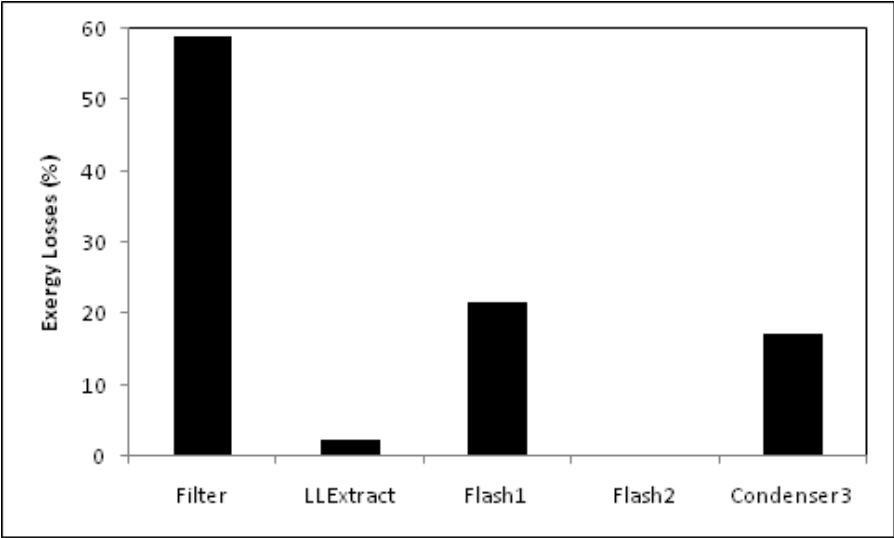


Table captions

Table 1. Reactions used to represent the lignin precipitation module included in biomass fractionation stage.

Table 2. Reactions used to represent lignin depolymerization.

Table 3. Inlet and outlet parameters (Temperature (°C), pressure (bar) and mass flow, F, (kg/h) for the energy flow, EF, (kW) calculations of the whole process.

Table 4. Exergy balance for the main streams.

Table 5. Exergy losses of the main equipment.

Table 6. Purchased equipment costs of the studied process.

Table 7. Annual operating and maintenance costs for the reference year 2016 (Sadukhan et al, 2014).

Table 8. Levelized costs of the studied plant.

Table 1.

Reactions	
Lignine (dissolved)	→ Lignine (solid)
Cellulose (dissolved)	→ Cellulose (solid)
Cellulose (dissolved)	→ Cellulose (solid)
Hemicelluloses (dissolved)	→ Hemicelluloses (solid)
Ash (dissolved)	→ Ash (solid)

Table 2.

Reactions	Yield (%)
Lignin (dis) → 0.075Oil + 0.026 Catechol + 0.004 Tar + 0.789 CH ₃ COH + 0.33H ₂ O + 0.908C	1
Cellulose (dissolved) + 3H ₂ O → 4CH ₃ OH + 2CO ₂	1
Hemicelluloses (dissolved) + 2H ₂ O → 3CH ₃ COH + CO ₂ + CO	1

Table 3.

Process stage	Stream	F (kg/h)	T (°C)	P (bar)	EF (kW)	
Stage (1)	Inlet streams	Biomass	106.5	25.0	1	143.5
		Solvent	600.0	25.0	1	1495
		Washing solvent	118.9	25.0	1	296.1
		Washing water	388.7	25.0	1	1710
		Water	758.4	25.0	1	3337
	Outlet streams	Condensates	380.8	78.8	1	841.2
		Cellulose	60.37	25.4	1	21.64
		Waste water	388.7	25.4	1	1699
		Filtrate	1124	26.5	1	4320
		Lignin	12.97	26.5	1	47.37
Stage (2)	Inlet streams	Lignin	12.97	26.5	1	47.37
		NaOH	259.4	25.0	1	1116
		HCl	27.39	25.0	1	83.05
	Outlet streams	Cond. 1	27.68	72.2	1	117.9
		Cond. 2	73.48	96.1	1	313.7
Stage (3)	Inlet streams	Depolym. prods.	198.6	50.3	1	788.0
		Ethyl acetate	885.9	25.0	1	1339
	Outlet streams	Catechol	0.540	25.0	1	0.462
		Oil	2.570	25.0	1	4.021
		Solid residue	21.45	50.3	1	59.65
		Ethyl acet. res1	877.0	70.2	1	1388
		Ethyl acet. res2	29.22	73.7	1	44.75
		Water residue	0.670	5.69	1	1.071
Aqueous phase	153.1	19.5	1	640.0		

Table 4.

Process stage	Stream	Enthalpy (MJ/kmol)	Entropy (kJ/kmol·K)	Exergy (kW)	
Stage (1)	Inlet streams	Biomass	-285,8	-163.1	0.238
		Solvent	-282.0	-248.0	0.011
		Washing solvent	-282.0	-248.0	220.1
		Washing water	-285.8	-163.2	1348
		Water	-285.8	-163.1	3047
	Outlet streams	Condensates	-274.7	-250.6	554.3
		Cellulose	-286.8	-165.4	21.87
		Waste water	-285.8	-163.8	1338
		Filtrate	-287.2	-178.8	3867
		Lignin	-25.53	-68.4	0.162
Stage (2)	Inlet streams	Lignin	-25.53	-68.4	0.162
		NaOH	-285.7	-158.2	936.5
		HCl	-242.3	-123.9	70.72
	Outlet streams	Cond. 1	-234.6	-59.27	91.18
		Cond. 2	-238.9	-37.09	256.0
		Depolym. prods.	-283.5	-156.3	636.9
Stage (3)	Inlet streams	Depolym. prods.	-283.5	-156.3	636.9
		Ethyl acetate	-480.2	-492.9	937.6
	Outlet streams	Catechol	-335.3	-412.8	0.293
		Oil	-308.0	310.4	0.892
		Solid residue	-301.4	-63.40	27.87
		Ethyl acet. res1	-410.2	-317.3	1000
		Ethyl acet. res2	-425.2	-335.5	32.19
		Water residue	-458.6	-459.7	0.757
		Aqueous phase	-289.5	-169.8	530.9

Table 5.

Equipment	Exergy in (MW)	Exergy out (MW)	Exergy losses (kW)
Stage (1)			
Mixer	0.004	0.011	7.270
Heat 1	1.135	1.106	28.34
Delignification	1.106	1.127	21.24
Flash	1.127	1.143	15.20
Condenser	0.598	0.618	20.72
Cooler	0.545	0.548	3.440
Filter 1	0.548	0.548	0.000
Tank	0.757	0.757	0.068
Precip	3.540	3.538	1.637
Washer 1	0.233	0.233	0.008
Washer 2	1.351	1.352	0.275
Filter 2	3.538	3.538	0.162
Stage (2)			
Mixer	0.936	0.936	0.006
Heat 2	0.936	0.908	28.51
Depolymerisation Reactor	0.908	0.916	8.241
Flash 1	0.916	0.916	0.473
Condenser 1	0.091	0.099	8.120
Flash 2	0.825	0.832	7.020
Condenser 2	0.255	0.265	9.780
Cooler	0.576	0.578	1.991
ACID	0.649	0.637	12.20
Precip	0.637	0.636	0.395
Stage (3)			
Filter	0.636	0.664	27.87
L-LExtraction	1.574	1.575	1.070
Flash 1	1.044	1.034	10.19
Flash 2	0.034	0.034	0.105
Condenser 1	1.000	1.008	8.082
Condenser 2	0.032	0.032	0.021
Dist column 1	0.001	0.001	0.014
Dist column 2	0.001	0.001	0.003

Table 6.

Equipment	Purchase equipment cost (PEC_k), (\$)
Stage (1)	
Tank	3900
Heat 1	8700
Delignification Reactor	46900
Flash	19500
Condenser	45000
Filter 1	6780
Cooler	8500
Precip.	8600
Washer 1	93800
Washer 2	93800
Filter	6780
Stage (2)	
Mixer	32100
Heater 2	8600
Depolymerisation reactor	33400
Flash 1	32500
Condenser 1	3900
Flash 2	23500
Condenser 2	8200
Cooler	8200
ACID	28000
Precip.	28000
Stage (3)	
Filter	6780
L-L Extraction	65000
Flash 1	15500
Flash 2	15500
Condenser 1	3900
Condenser 2	3900
Distillation column 1	37600
Pump 1	3900
Distillation column 2	34800
Pump 2	3900
Cooler 1	8200
Pump 3	3900
Cooler 2	8500
TOTAL (PEC_T)	760040

Table 7.

Designation	Cost (M\$)
Fixed annual operating and maintenance costs	5.22
Variable annual operating and maintenance costs	0.52
Total annual operating and maintenance costs	5.75

Table 8.

Designation	Cost (\$)
The levelized total required revenue (TRR_L)	15.95
The levelized fuel costs (FC_L)	0.12
The levelized operation and maintenance costs (OAM_L)	14.31
Carrying Charges (CC_L)	1.51