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Keywords: Lignin, Depolymerization, Simulation, Organosolv, Catechol

Techno-economic analysis of different integrated biorefinery scenarios using lignocellulosic waste streams as source for phenolic alcohols production

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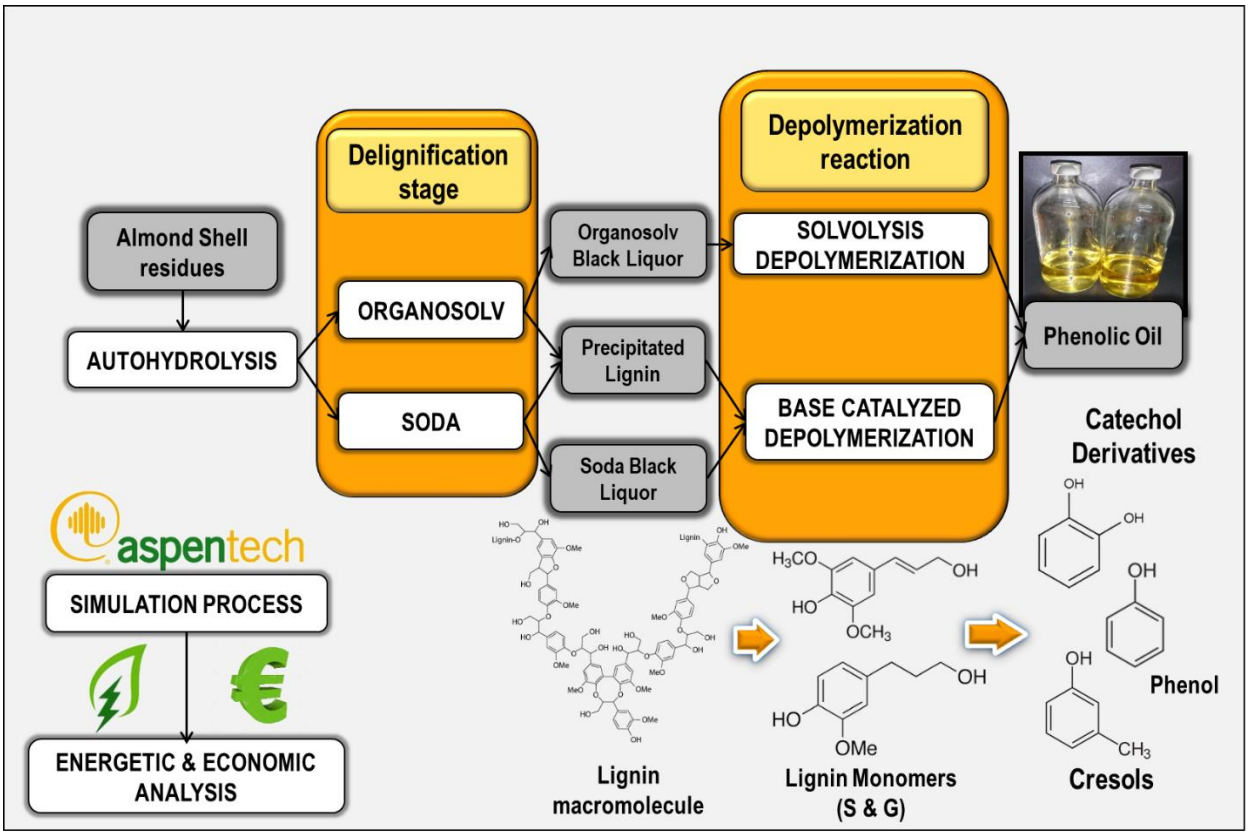
Graphical abstract



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1. Introduction

The interest in the lignocellulosic waste streams valorization has emerged in the last decades due to the potential of this feedstock to be converted into value-added products, such as fuel, chemicals and biomaterials. All these waste streams are considered low cost materials, for which, in some cases, a payment has to be done to remove them from the soils after the harvesting or their value is minute. Several approaches have been addressed to convert biomass feedstock into these value-added products, based on the fractionation into its main macro components: cellulose, lignin and hemicelluloses. This approach has been lately applied to create integrated biorefineries where several streams from biomass are valorized. (De Bhowmick et al., 2018).

The soda and the organosolv processes can be emplaced in the center of the spectrum regarding biomass fractionation processes. They are not widely utilized at commercial level, as the traditional Kraft method nor are the most innovative processes to separate lignin from the carbohydrate platform of biomass, due to the loss of the intrinsic properties that fibers undergo when are submitted to these type of process, making them inadvisable to be used in the papermaking processes (Zhang et al., 2016). However, they offer a good compromise between a simple and environmentally friendly route to obtain lignin without the pollution of sulfur, which hinders its further conversion, keeping the carbohydrates compounds available to be converted into value-added chemicals (Fernández-Rodríguez et al., 2017b). The problem of this process is the competing reactions that occur in parallel, as for example the carbohydrates degradation (peeling) that leads to the production of lower quality of cellulosic pulps (Rinaldi et al., 2016). This is the main reason why it is not industrially used in the papermaking processes. Nevertheless, if the process is intended to reach products from the degradation of cellulosic fibers, such as nanocelluloses, the soda process could be highlighted as one of the most promising fractionation processes. The organosolv processes use organic solvents to solubilize lignin without altering its initial structure in high degree. Some alcohols, such as methanol or ethanol are the most common solvents used in these methods, although a wide range of solvents are also being studied for this purpose (Azadi et al., 2013). The main drawback of this process is the high cost of these solvents, although this disadvantage can be minimized by recovering and recycling them through evaporation and condensation (Kumar and Sharma, 2017), but also the safety constrains due to the utilization of flammable solvents.

One of the most interesting topic for the scientific community to valorize lignin has been its utilization as source to obtain fine chemicals by its depolymerization into smaller structures, as phenolic monomer compounds (Montazeri and Eckelman, 2016). Several type of reactions has been approached for this purpose: reductive, oxidative, base/acid catalyzed, solvolytic, thermal and enzymatic depolymerization are between those examples (Schutyser et al., 2018). Base catalyzed depolymerization (BCD) is one of the most studied process due to its balance among simplicity and efficiency. The reaction is based on the cleavage of lignin ether bonds, main linkages of lignin, which are polarized to reduce the required energy in its scission. The phenolic oil generation is hampered due to the repolymerization reactions that occurs when unstable intermediates of the reaction trend to condensate again through formation of carbon-carbon bonds. Under relative low temperatures (<300 ºC), methoxyphenols are the most commonly obtained monomers whereas when reaction is developed at harsh conditions (>300 ºC), the selectivity tunes to catechol and alkylcatechols. Solvolytic depolymerization of lignin appears as an alternative process, where reaction yields are lower and methoxy-products are the most common compounds obtained by this procedure (Katahira et al., 2016).

These lignin-based products must be competitive with their petroleum-derived counterparts. At this point, it is very important to design energetically efficient process for the lignin extraction and purification. Otherwise, it would be difficult to offer an actual alternative to consolidated products based on fossil resources (Mabrouk et al., 2016). For this purpose, lignin-based products have to be assumed as a section of an integrated biorefinery where multiple products are obtained and in this line being able to compete in a realistic scenario. This bring the necessity to implement advanced synthesis methods that allows the integration and optimization methods to guarantee the economic feasibility with lower environmental impact (Martín and Grossmann, 2013). Techno-economic evaluation of the global process should involve both, the identification of primary cost drivers, as well as the feasibility to scale them to the industrial

level (Biddy et al., 2016). Several researches can be found in the literature about the simulation of biorefinery processes for the design of manufacturing processes to obtain value-added chemical from lignocellulosic resources. Moncada et al. (2018) evaluated the production of C6 sugars from softwood and corn feedstock, approaching two techniques: organosolv of spruce and corn wet mill. Nhien et al. (2017) proposed a hybrid extraction/distillation process to produce furfural. The simulation process allowed evaluating different solvents to find the most suitable alternatives. However, few of them are considering the whole integrated biorefinery approach. Celebi et al. (2017) developed a systematic methodology to design an integrated biorefinery which utilized wood as feedstock to obtain C5 and C6 carbohydrate monomers, lignin and syngas products. Nitzsche et al. (2016) assessed the conversion of beech wood into different chemical products (ethylene, organosolv lignin, bio methane and hydrolysis lignin) by simulating the process. In the same line Zang et al. (2020a) developed an integrated biorefinery process with deep eutectic solvents to obtain furfural from the carbohydrate platform and technical lignin with positive economic results by using switchgrass as feedstock and the same approach and results were also applied by Zant et al. (2020b)to obtain furfural by one-pot process. Lignin-based products were addressed in other manuscripts, as Shen et al. (2019) that used the NREL data source to create an integrated process to obtain ethanol from the carbohydrate platform, and jet fuel from lignin. The results showed that the obtaining of paraffins from lignin is still not economically competitive. The influence of the precipitation stage on an integrated process following the “lignin-first” approach, was evaluated by the techno-economic analysis carried out by Chrisandina et al. (2019), concluding the difficulties to currently commercialize technical lignin obtained by this approach. In a previous work of the research group, a deep analysis of energetic and economic analysis was already proposed from an experimental work, where only the last part of the valorization process of lignin for the catechol production was assessed by the alkaline degradation of lignin with promising results (Mabrouk et al., 2018).

In this work, the scaling of an integrated fractionation process from laboratory experiments to industrial scale was addressed by means of a chemical simulation software. Despite the experiments were focused to lignin-based products, the scaling process has been conducted taking into account all the different platforms from biomass. The objective was targeted on the design of an integrated biorefinery mainly focused on the phenolic products that can be obtained by the lignin depolymerization, but also considering the cellulosic pulp which is obtained during the process. The modeling was carried out matching the chemical pathways undergone in the experiments to build up a simulation model as much realistic as possible. Different scenarios were approached to compare the influence of several variables, such as the delignification stage, or the introduction of intensification stages in the process. Furthermore, the impact of these changes was techno-economically analyzed. In this way, the most suitable route in terms of product efficiency, waste reduction and energy and economic performance was identified to optimize the whole integrated biorefinery processes. Thereby, this work provides a comprehensive study of an integrated biorefinery scheme taking into account not only the carbohydrate fraction of the biomass but also the production of phenolic compounds from the lignin stream.

2. Materials and methods

This work is based on other previous experimental works where the influence of the delignification method on the lignin depolymerization products (Fernández-Rodríguez et al., 2017a) and the impact of reducing the precipitation stages of lignin by its direct depolymerization from black liquors (Fernández-Rodríguez et al., 2020) were evaluated. Therefore, all the experimental values used in this work come from real data values obtained at laboratory scale. Aspen Plus® has been the software used in this work to develop the technical simulation of the different scenarios.

2.1. Lignin extraction process design

In this first section (S1), two different scenarios were assessed. Almond shells were selected as the lignocellulosic waste feedstock and two delignification processes were compared: organosolv and soda processes. The composition of the initial raw material is described in the Supplementary data (Table S1). This material was subjected to an auto hydrolysis pre-treatment to increase the lignin concentration prior to the delignification stage. The reaction was carried

out at 180 ºC, using only water as reagent in a 1:8 solid/liquid ratio. After this stage, the solid material was cleaned and driven to a pulping stage where lignin was extracted. The organosolv pulping was conducted using a mixture of ethanol/water (70/30 V/V) at 200 ºC in a 1:6 solid/liquid ratio, whereas the soda process was carried out at 121 ºC using a NaOH 7.5 wt.% solution as reagent in the same solid/liquid ratio as in the organosolv method. Regardless the used process, the undissolved solid was cleaned in two steps: first with the same solvent utilized in the reaction; and then with water to obtain a cellulosic pulp. On the other hand, the black liquor obtained after the reaction was subjected to a precipitation stage. In the organosolv process lignin was precipitated with the addition of 2 volumes of acidified water (pH = 2), and then filtered to obtain lignin as the solid fraction. For the soda black liquor, the lignin was precipitated by dropping the pH to 4 by the addition of H_2SO_4 (96 wt.%). The filtered cake was then washed with water to remove the excess of salts generated by this precipitation method.

2.2. Lignin depolymerization

After its isolation, the lignin samples were subjected to a depolymerization process to obtain small phenolic compounds. In this second section (S2), two reaction mechanism were approached: the depolymerization of the solid lignin samples, but also the depolymerization of the lignin contained in the black liquors without its previous isolation by the precipitation stage. In the first case, the precipitated lignin samples were subjected to BCD using NaOH 4 wt.% as catalyst at 300 ºC in a 1:20 solid/liquid ratio. In the second approach, the liquors were driven to 300 ºC. This fact means that two different reaction mechanisms were approached: (i) solvolysis of the lignin for the organosolv black liquors, and (ii) base catalyzed depolymerization for the soda black liquors.

The undesirable byproduct of this reaction (tar) was removed by acid precipitation, and the phenolic oil was extracted by a liquid-liquid extraction using ethyl acetate as organic solvent. Finally, the solvent was recovered by distillation. The whole process is depicted in Figure 1.

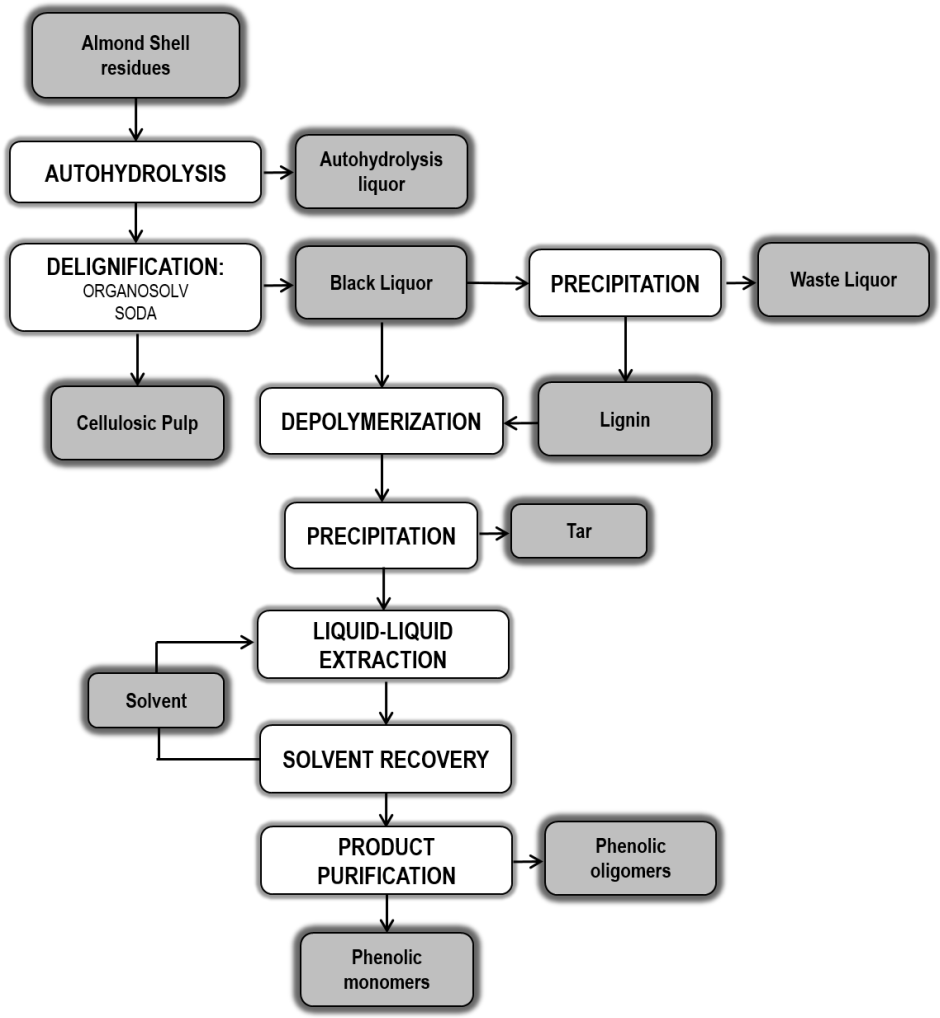

Figure 1. Description of the lignin extraction and conversion process into small phenolic compounds.

2.3. Simulation by computer-aid software

Based on the processes described above, the simulation was built up by Aspen Plus® (V10) software. The flowsheets where divided in two sections. Non-Random Two-Liquid-Redlich-Kwong (NRTL-RK) model was selected to simulate the thermodynamic properties of the streams involved in the process. The simulation of the first section of lignin extraction used as basis 100 kg/h of dry raw materials as initial point. All the parameters for the design of the different units involved in S1 for both scenarios are depicted in the Supplementary data (Table S2).

2.3.1. Modelling of S1

Almond shells were submitted to the auto hydrolysis pretreatment, defined by a stoichiometric reactor. The biomass dissolving reactions were defined by the next reactions:

1) Cellulose (s) → Cellulose (d)
2) Cellulose (d) + H_2O → Glucose (d)
3) Xylan (s) → Xylan (d)
4) Xylan (d) + H2O → Xylose (d)
5) Lignin(s) → α Lignin1(d) + β Lignin2(s)

6) Extractives(s) → Extractives(d)
7) Ash(s) → Ash(d)

The solid cellulose (s) was firstly converted into dissolved cellulose (d). After that, this cellulose (d) was hydrated to form glucose (d). In a similar way, the hemicelluloses which were defined as xylan (s), were partially transformed into xylose (d). The lignin (s) contained in the biomass was converted into dissolved lignin1 (d) and other fraction remained in the pulp as lignin2 (s). The molecular formula of lignin (s) contained in the solid and lignin1 (d) were defined using a previous work developed in the research group (Mabrouk et al., 2018). The lignin2 (s), whose composition differs with regard to the original one, was calculated to satisfy the mass balance of the reaction. The conversion index was fixed to the unit and the product yields were fixed by the stoichiometric factors (α and β). The extractives were assumed to be exclusively formed by β-sitosterol, following the same procedure than in other works (Freire et al., 2006). The ash content was defined as CaO to simplify the simulation. All the yields for each reaction or stoichiometric factors were obtained from the experimental section, whose values are detailed in the Supplementary data (Table S3)

In the organosolv process, the solid fraction was mixed with a stream of ethanol:water (70/30 v/v) in a liquid:solid ratio of 6:1. The stream was heated up to 200 ºC and driven to a stoichiometric reactor. The reactions that took place in this reactor were the same that the ones defined for the auto hydrolysis reactor, although the yields were notably different, as it can be seen in the Table 2 as well. The only exception was the reaction Nº 5, whose description is as follow:

5) Lignin2 (s) → α Lignin2 (d) + β Lignin3 (s)

The obtained stream was driven to a flash unit to reduce the pressure until atmospheric level as well as to recirculate the condensed stream, which was mainly composed by ethanol (~80 %). The lignin contained in the black liquor was precipitated by adding acidified water (H_2SO_4 96 wt.%). The flow of this stream was designed to be 2 times the flow of the total black liquor stream. During the precipitation, whose simulation was defined by a stoichiometric reactor, the following reactions took place:

1) Lignin2 (d) → Lignin4 (s)
2) Xylose (d) → Xylan (s)
3) Ash (d) → Ash (s)

The conversion factor of reaction Nº1 was defined by the experimental section. However, the reactions Nº2 and Nº3 were defined by means of design of specifications to reach the exact composition of the lignin samples that were obtained in the previous work (Fernández-Rodríguez et al., 2017a). These values are detailed in the Supplementary data (Table S4).

In the organosolv method the liquid fraction was submitted to a recuperation stage, where the solvent was distillated to be recirculated to the delignification reaction. The reflux ratio and the number of stages were fixed to 1.5 and 5, following the methodology described in a previous work of the research group (Mabrouk et al., 2018), whereas the distillated to feed ratio was designed by a design of specification to obtain a final condensate stream, whose composition would contain 70 wt.% of ethanol (same than solvent used in the delignification stage). In this way, the ethanol consumption was reduced in a 95.8 %, i. e., to an almost negligible quantity. The final flowsheet of the organosolv lignin extraction section is presented in Figure 2.

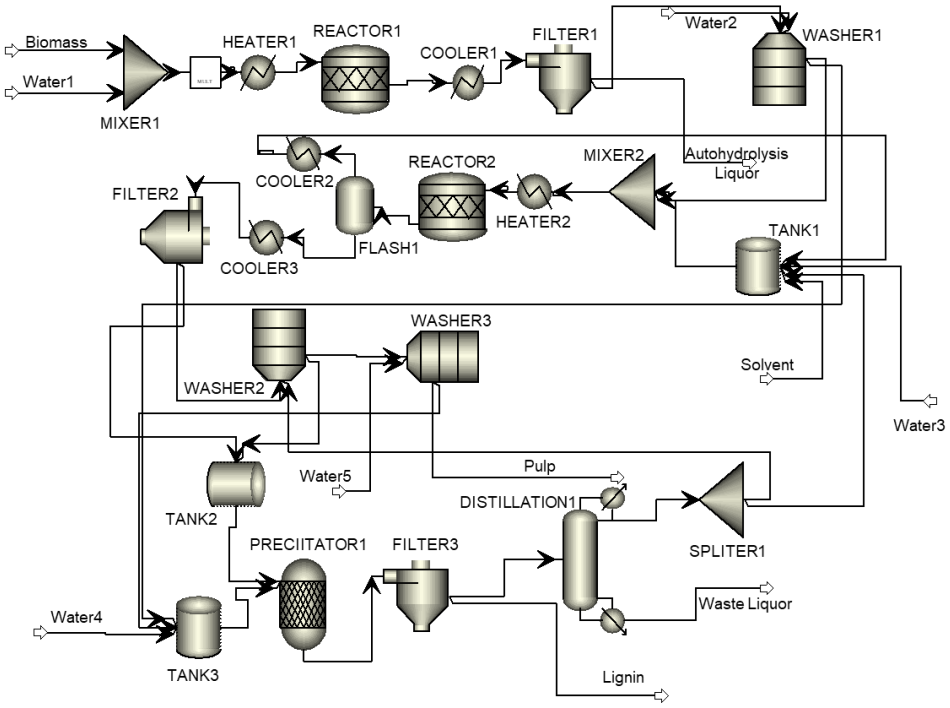

Figure 2. Flowsheet of S1 for the organosolv process.

In the case of the soda process, the solid fraction submitted to the delignification stage was mixed with soda (7.5 wt.%) in a liquid:solid ratio of 1:6. The reactions were introduced in the same format than in the organosolv process. The differences were based on the reaction yields that were also included in Table 2. However, the temperature of this reaction was noticeably lower (121 ºC).

The final black liquor was submitted to the lignin precipitation stage. The reactions of this stage were the same than in the organosolv process although the conversion factors were adjustment to obtain the same final composition of the lignin sample obtained in the experimental work, with an acid precipitation at pH = 4 (Fernández-Rodríguez et al., 2017a). The precipitation of the lignin was accomplished by adding H_2SO_4 (96 wt.%) in excess to neutralize the [OH-] ions and generate an acid medium (pH = 4). This excess was defined by a design of specification. The new reaction (Nº4) was introduced in this unit as follow:

4) $2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$

In this scenario there was not a recovery stage for the used solvent. A schematic representation of the soda lignin extraction process is represented in Figure 3.

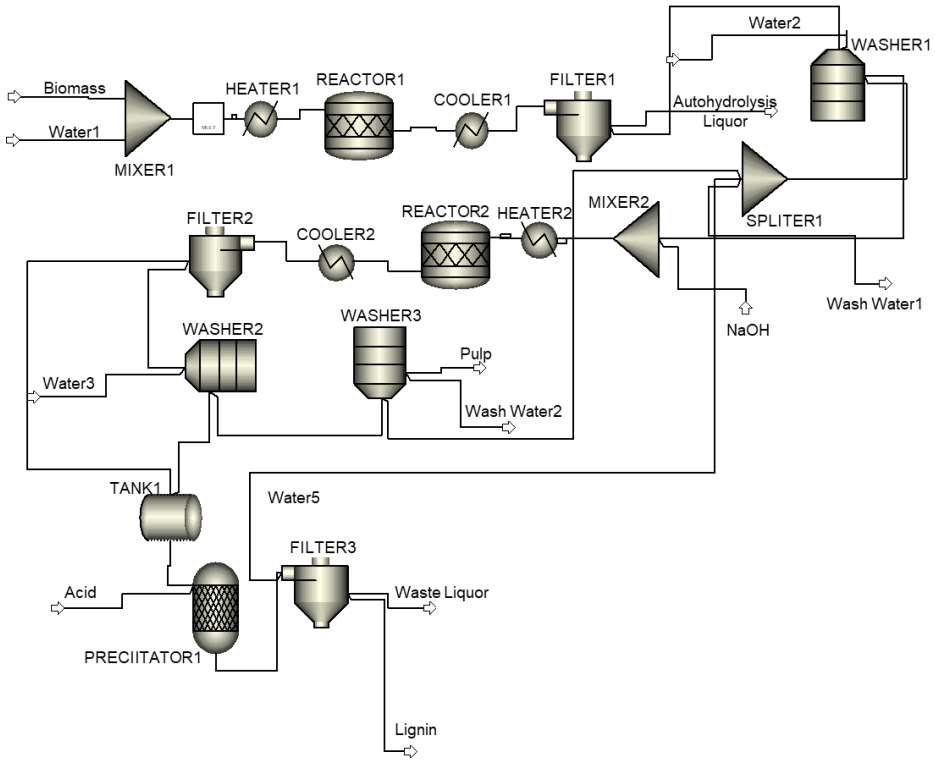

Figure 3. Flowsheet of S1 the soda process.

2.3.2. Modelling of S2

In this section, two scenarios were approached for each lignin extraction process: (i) the depolymerization from the isolated lignin samples (AOS and ASS), and (ii) the direct lignin depolymerization from the black liquors (AOL and ASL). All the parameters for the design of the different units involved in S2 are showed in the Supplementary data (Table S5).

In the first option, the process started with the mixture of the lignin and NaOH (4 wt.%) in a unit defined as a stoichiometric reactor, whose reactions were exactly the opposite from the ones described for the precipitation stage. This mixture was submitted to the depolymerization reactor with a previous heating up to 300 ºC. The depolymerization reactor was also defined as a stoichiometric reactor, where the following reaction took place:

1) Lignin4 (d) $\rightarrow$ α Phenol + β Catechol + χ Cresol + δ Guaiacol + ε Syringol + ϕ Oil + γ Tar + η Methanol
2) 0.6 Xylan (d) + 1.6 H_2O $\rightarrow$ 2 Methanol + CO_2

The phenolic oil and the tar properties were defined from a similar literature work (Beauchet et al., 2012). The conversion for the reaction Nº1 was fixed as total and the product conversion factors were defined by the stoichiometric factors required to obtain the same yield as in the experimental sections. The methanol conversion factor was adjusted to guarantee the molar balance of the reaction. All the conversion yields or stoichiometric factors are detailed in the Supplementary data (Table S6).

After the reaction and before the cooling, the pressure was released using two flash separation units. In the first unit, the pressure was reduced to 50 bar and it reached 1 bar in the second one. In these units, two gaseous streams were generated; whose compositions were mainly water and methanol. In fact, the methanol was totally removed from the circuit by these streams. Once the pressure was set to the atmospheric level, the liquid stream was cooled down to 25

ºC and driven to a precipitator to remove the tar produced during the reaction by the acidification until pH = 2 with HCl. This stage was defined as a stoichiometric reactor as well, where the following reaction took place:

1) Tar (d) → Tar (s)
2) Ash (d) → Ash (s)
3) NaOH + HCl → NaCl + H_2O

The HCl quantity was fixed by a design of specification as the required amount to reach a pH = 2 in the medium after the reaction. All the conversion factors were established as the unit, e. i., a total precipitation was assumed in this stage.

The liquid fraction was driven to a liquid-liquid extraction operation. In this stage, a flow of ethyl acetate was fixed as 5 times the flow of the fed stream, in order to extract the phenolic oil from the aqueous stream. Then, two distillation columns were needed to separate the phenolic oil fraction from the ethyl acetate. Both columns were defined by 5 stages with a reflux ratio of 1.5, as in the previous distillation column. However, the distillate to fed ratio parameter was set by a design of specification to reach a percentage of separation for the ethyl acetate of 99.5 wt.% and 99.9 wt.%. The collected ethyl acetate from the distillated streams was recirculated to the liquid-liquid extraction column to minimize the consumption of this component. With this recirculation, only 1.15 % of the initial required quantity was necessary to be fed in the system. Finally, the separation of the phenolic oligomers and the phenolic monomers was also conducted by an additional distillation column. In this unit, 5 stages and a reflux ratio of 1.5 were also fixed following the methodology described by Mabrouk et al. (2018). However, the distillated to fix ratio parameter was designed by a design of specification to reach a concentration in the distillated stream higher than 95 wt.%. A schematic representation of the lignin depolymerization and the product separation (S2) processes is represented in Figure 4.

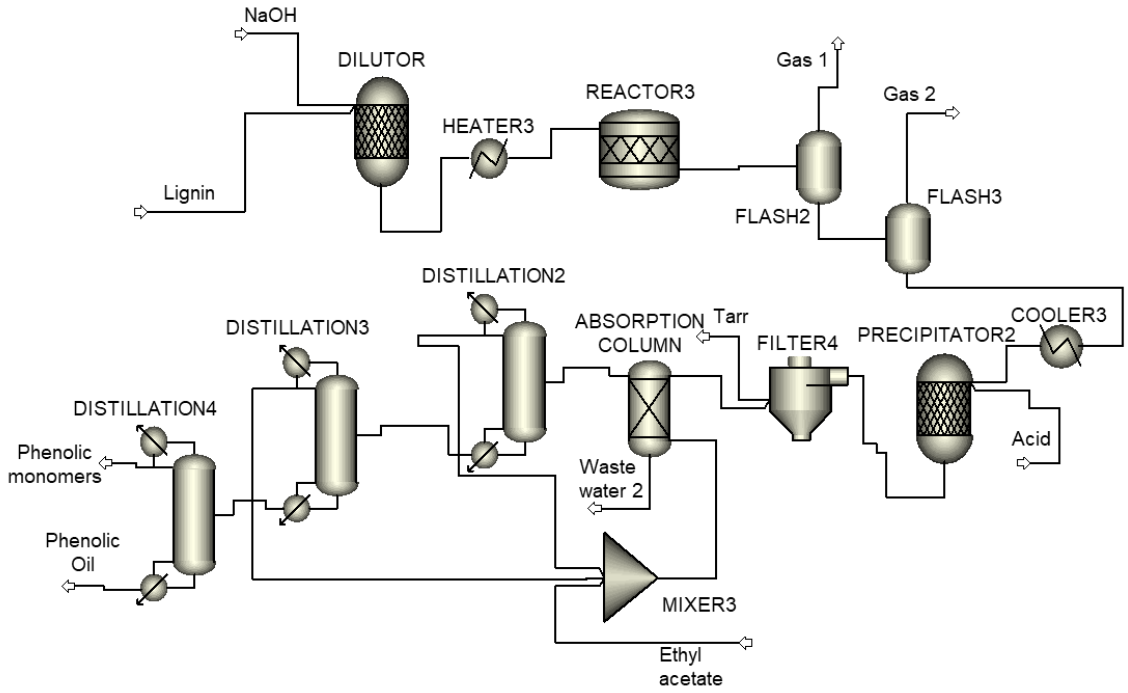

Figure 4. Flowsheet of the S2 for lignin depolymerization and phenolic monomer products purification.

2.4. Energy integration analysis

The performance of the chemical processes cannot be evaluated only by mass balances and the product yields. Energy also plays an important role in the production cost of processes; thus, the energy requirements must be also considered. In this work, the energetic demands of all proposed flowsheets were analyzed using Aspen Energy Analyzer® software. The base simulation considered that all the energy demands were applied from utilities streams. The streams data, such as flows, temperatures and enthalpies are used by the software to quantify the possibilities of energy saving by the integration of heat from different existing streams, following the methodology of the "pinch" analysis, which is considered as the most widely used technique to calculate the maximum thermodynamically feasible targets in energetic integration (Kemp, 2007).

2.5. Economic analysis

The economic assessment was carried out to compare the different scenarios developed by the simulation process, as well as the current situation in a hypothetical real market situation. The purchased and installed equipment costs (BMC) were calculated by the principle of "economies of scale" (Equation 2.1) as it was also employed by Sadhukhan et al., (2014). Most of the equipment costs were scaled from similar previous works (Hamelinck and Faaij, 2002; Jones et al., 2009; Loh et al., 2002; Ng and Sadhukhan, 2011a, 2011b) and updated to the cost of the current year (2017) by the Equation 2.2, using the chemical engineering plant cost indexes (CEPCI).

$$\frac{COST_{size2}}{COST_{size1}} = \left(\frac{SIZE_2}{SIZE_1}\right)^R \quad \text{(Eq. 2.1)}$$

Where $SIZE_1$ is the capacity of the base system, $COST_{size1}$ is the cost of the base system, $SIZE_2$ is the capacity of the system after scaling up/down, $COST_{size2}$ is the cost of the system after scaling up/down, and R is the scaling factor.

$$C_{pr} = C_o \left(\frac{I_{pr}}{I_o}\right) \quad \text{(Eq. 2.2)}$$

Where C_{pr} is the present cost, C_o is the original cost, I_{pr} is the present index value, and I_o is the original index value.

The Fixed Capital Invested (FCI) was estimated using the on-site costs, obtained by the Guthrie's method (Biegler et al., 1997), taking into account the off-site and indirect costs, the working capital and the plant startup cost as it is detailed in Table 1. The Manufacturing Costs (COM) were estimated considering the operating labor cost (C_{OL}), the costs of utilities (C_{UT}), the waste treatment cost (C_{WT}); and the cost of raw materials (C_{RM}) (Turton et al., 2013).

Table 1. Description of estimated parameters calculated in this work.

Parameter	Calculation/Value	Reference
FCI	**1.3·Fixed Capital**	(Biegler et al., 1997)
On-site Cost	BMC	(Biegler et al., 1997)
Off-site Cost	0.45· On-site Cost	(Biegler et al., 1997)
Indirect Cost	0.25·(On-site + Off-site)	(Biegler et al., 1997)
Fixed Capital	On-site + Off-site + Indirect Cost	(Biegler et al., 1997)
COM	**$0.28 \cdot FCI + 2.73 \cdot C_{OL} + 1.23 \cdot (C_{UT} + C_{WT} + C_{RM})$**	(Biegler et al., 1997)
Operating Labor Cost		
Operators Salary	$41{,}600 \cdot (1.03)^{(\text{Current year}-2003)}$	(Peters et al., 2011)
Utilities Cost		

Cool water	8.67E-05 €/kg	Local mill
Low pressure steam	1.1E-02 €/kg	Local mill
Medium pressure steam	1.12E-02 €/kg	Local mill
High pressure steam	1.45E-02 €/kg	Local mill
Furnace heat	2.46E-02 €/kg	Local mill
Waste treatment Cost		
Waste water treatment	0.08 €/m^3	(Moncada et al., 2018)
Raw material Cost		
Biomass	0.052 €/kg	(Sharifzadeh and Shah, 2015)
NaOH	0.4 €/kg	Local mill
Ethanol	0.61 €/kg	(Celebi et al., 2017)
Ethyl acetate	0.72 €/kg	(Straathof and Bampouli, 2017)
HCl	0.15 €/kg	Local mill
H_2SO_4	0.04 €/kg	Local mill

3. RESULTS AND DISCUSSION

The different scenarios were analyzed by a holistic approach taking into account the mass and energy balances as well as their economic performance, as it is detailed below.

3.1. Mass balance analysis

The process efficiency was evaluated in terms of water and chemicals (ethanol or soda) consumptions and total energy duties required to develop the process of lignin extraction. Main parameters of the process are detailed in Table 2.

Table 2. Process efficiency in terms of product yields, water, chemicals and waste streams.

Parameter	Units	Organosolv	Soda
Lignin yield	%	4.89	10.21
Pulp yield	%	55.21	38.19
Solvent consumption	kg/h	14.65	427.3
Water consumption	kg/h	1,372	946.9
Waste Streams	kg/h	1,433	1,391
Acid	kg/h	-	75.84

The product yields, referred to the initial biomass introduced to the system, were clearly influenced by the extraction method. The soda process highlighted its major facility to solubilize biomass despite its lower severity factor (121 ºC for soda process against 200 ºC for the organosolv method). Consequently, the solid fraction (pulp), presented lower yield and the recovered lignin was higher, since it is the main product solubilized from the solid fraction. This difference

was significant, as the lignin yield for the soda process doubled the yield obtained in the organosolv process; whereas for the cellulosic pulp, the yield was around 30 % lower. Therefore, the delignification process could be selected depending on the product that was tried to be maximized. The experimental process was focused on the lignin-base product, which means that the cellulosic pulp yield was higher for the organosolv process, although the quality of this pulp was not assessed in the reference works.

The inclusion of the distillation column in the organosolv process leaded to an extremely lower solvent consumption. Specifically, the consumption of solvent for the organosolv method was less than 5 % in comparison with the soda process, remarking the sustainable character of the organosolv process. However, the water consumption was greater when organosolv method was used. This fact was owing to lignin precipitation stage, where big volumes of water were consumed in the organosolv method (double volume than the black liquor), whereas only low quantities of acid were used in the soda process. This involves a 40 % more water was consumed in the organosolv process. As a consequence of the water consumption, higher volume of waste streams was also created in the organosolv process. However, this difference was reduced because of the greater volume of black liquor created during the soda reaction, where more biomass was solubilized into the liquid stream. One of the main drawbacks of using the soda method instead of the organosolv one, was the necessity of including high volumes of strong acids during the process in comparison with the initial biomass stream.

The evaluation of the S2, which consisted in the lignin depolymerization and the product separation by different downstream stages according to the flowsheet depicted above, was assessed by the results showed in Table 3, where flows of main output streams were detailed and expressed using lignin stream as the fed stream (100 kg/h) or initial biomass as reference stream (100 kg/h as well).

Table 3. Process efficiency in terms of product yields, water, chemicals and energy consumption as well as waste streams (OS: Organosolv Solid lignin depolymerization; OL: Organsolv Liquor depolymerization; SS: Soda Solid lignin depolymerization; SL: Solid Liquor depolymerization.

	Parameter	Units	OS_1	OS_T	OL_1	OL_T	SS_1	SS_T	SL_1	SL_T
Inputs	Lignin	kg/h	100.0	4.9	100.0	5.8	100.0	10.2	100.0	11.9
	NaOH	kg/h	1,894	92.6	-	-	1984	202.1	-	-
	Acid	kg/h	331.2	16.2	1,404	81.0	216.9	22.1	1,310	155.7
	Ethyl acetate	kg/h	108.3	5.3	147.6	8.5	62.6	6.4	139.7	16.6
Outputs	Phenolic monomers	kg/h	1.60	0.08	1.42	0.08	0.30	0.03	0.46	0.05
	Phenolic oil	kg/h	54.09	2.64	27.76	1.60	9.80	1.00	32.46	3.86
	Tar	kg/h	32.15	1.57	69.92	4.03	35.14	3.58	66.41	7.89
	Waste water	kg/h	1,233	60.3	1,404	81.0	1,137	115.9	2,648	314.7
	Gas	kg/h	981.9	48.0	5,448	314.3	1,050	106.9	1,753	208.3

1: output stream flows referred to 100kg/h of lignin fed to section 2.

T: results referred to 100 kg/h biomass.

**OL tar precipitation was carried out using acidified water (2 volumes), not HCl as other reactions.*

The variations in consumed raw materials already demonstrated the huge difference between the lignin depolymerization from precipitated lignin and the direct lignin depolymerization from the spent black liquor. The high soda/lignin ratio used in the experiments (20:1) provoked a great consumption of soda in the precipitated lignin

depolymerization reaction. Despite this fact, the precipitation of lignin prior to its depolymerization led to work with lower volumes, which had a big influence on the acid and ethyl acetate consumptions, showing higher acid consumption for the direct depolymerization processes.

Except in case of the OL depolymerization, the main products obtained in the phenolic monomers stream were catechol and catechol derivatives (considered as same group to facilitate the interpretation), with a selectivity higher than 95 %. In the case of OL depolymerization, a mixture of monomers was obtained, where syringol was the most plenty product (>50 %), followed by guaiacol (<25 %) and catechol derivatives (>15 %), emphasizing the different reaction mechanism experimented by the solvolysis mechanism instead of the base catalyzed depolymerization. In terms of the reaction yields, OS and OT scenarios showed not only better depolymerization yields, but also higher yields referred to the original biomass. Despite the lower yield of the lignin extraction from biomass, the global yield to depolymerize lignin was finally better for the organosolv process. This suggests that the organosolv lignin presented a more suitable structure to be depolymerized than in the case of the soda lignin as it was already pointed by a previous work (Fernández-Rodríguez et al., 2020). Indeed, more phenolic oil was obtained for the SL scenario than for the OL one, despite the lower phenolic monomers quantity obtained in SL. Regarding the influence of avoiding the precipitation stage, it was remarkable the results obtained in the organosolv scenarios, since the total yield, referred to the initial biomass, of the OL_T scenario was the same as in the OS_T scenario. This is due to the bigger lignin amount that was fed to the depolymerization process when precipitation stage was removed, since the suppression of this stage noticeably reduced the loss of lignin in the section between the delignification stage and the lignin depolymerization reactor. On the other hand, the removal of the precipitation stage in the soda process led to an increase in the depolymerization reaction yields, probably due to the extremely low yield obtained in SS reaction. The direct lignin depolymerization provoked clear benefits for most interesting products: phenolic monomers plus phenolic oil in the case of the soda process. Tar, a byproduct of the depolymerization reaction formed by a mixture of repolymerized and depolymerized lignin fractions, was produced in higher quantities by in the direct depolymerizations, regardless the delignification method. The lignin depolymerization rate was faster from liquors, as well as the formation of unstable intermediate products that are prone to repolymerize. In this line, the inclusion of capping agent to stabilize those compounds prior to its depolymerization would be necessary in future studies.

Other negative impact of the direct lignin depolymerization was the higher waste water generated as output. If the lignin is not precipitated, more volume had to be treated and as a consequence, more water was finally discharged. The higher amount of waste streams was not the only drawback of using the direct depolymerization concept. As it was mentioned before, in the organosolv process it was not allowed recirculating ethanol by the inclusion of a distillation column. As a result, the increase of the solvent used for the organosolv reaction rose up from 14.65 kg/h to 245.5 kg/h. This fact was expected to hugely increase the raw material costs of this scenario.

The composition of the gas streams produced in the flash units was mainly steam that could be used for heating other streams in parallel to save energy. In the case of OL, these streams presented bigger volume due to the evaporation of the ethanol, what led to a decrease in the total flow of water disposal in comparison with the SL reaction. In further optimizations, the ethanol could be extracted from these streams to be recirculated to the system to reduce its consumption. However, such stage would be complicate to implement due to the high level of trace compounds also contained in these streams.

3.2. Energetic evaluation

The performance of the energetic duties for each scenario were directly calculated by Aspen Energy Analyzer® software. In this section, the total utilities demand, as well as the distribution of these demands by stage were analyzed. The energetic duties for each section are detailed in Table 4.

Table 4. Energetic duties for different scenarios (S1: Section corresponding to lignin extraction; S2.1: Section corresponding to lignin depolymerization from precipitated lignin; S2.2: Section corresponding to lignin depolymerization from black liquor; T: Accumulate values for the global process).

Section	Organosolv			Soda		
	Heating (kW)	Cooling (kW)	Total (kW)	Heating (kW)	Cooling (kW)	Total (kW)
S1	479	435	914	192	196	387
S2.1	107	118	225	279	213	492
S2.1T	587	553	1,140	470	409	879
S2.2	373	198	570	707	673	1,380
S2.2T	606	435	1,040	899	868	1,767

In the case of S1, the total energetic duties were strongly influenced by the inclusion of the distillation column for the solvent recovery on the organosolv process and the higher temperature required on the delignification stage. In general, more than the double of the energetic utilities was required for the organosolv process than in the case of the soda process.

In Figure 5 and Table 5, the distributions of those duties for S1 are detailed. It can be observed that 50 % of the total duties were caused by the distillation column (as sum of the reboiler and the condenser duties). The auto hydrolysis reaction was the second stage with the highest energetic demand, considering the combination of “Heater1” and “Cooler1”. This influence was more notorious for the soda process (four times higher than the delignification reaction, for instance) due to the temperature used in the delignification stage (121 ºC), in comparison with the organosolv process (200 ºC). The influence of the flow on the energetic demands was highlighted in the organosolv process, since even when the delignification reaction required a greater temperature than the auto hydrolysis pretreatment, the bigger flow to be treated in the pretreatment reaction led to a higher energetic duty (more than two times).

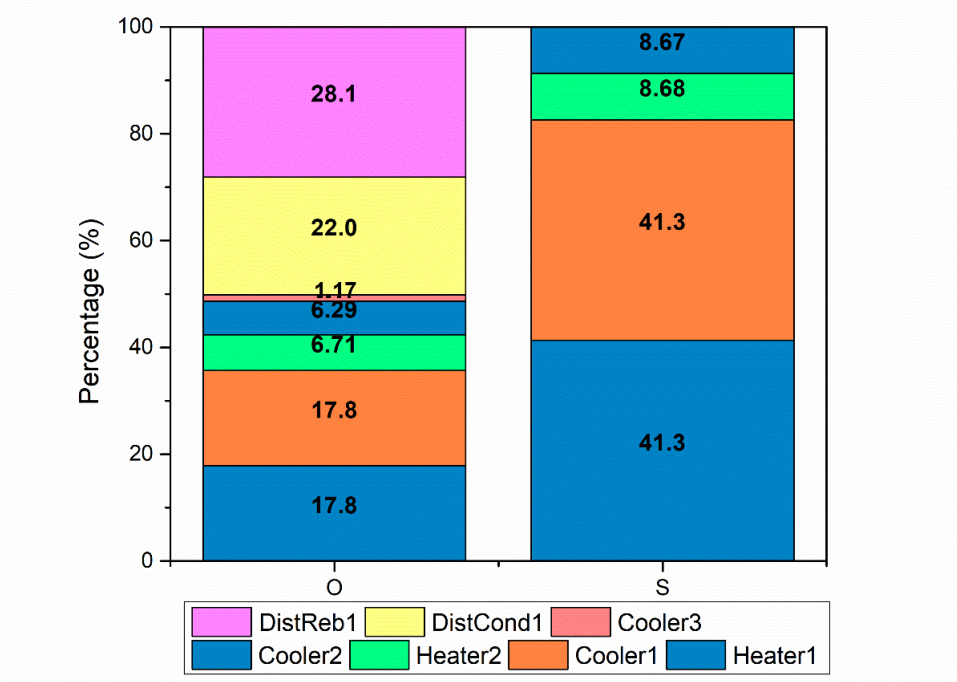

Figure 5. Distribution of energetic duties by unit for S1 scenarios.

Table 5. Energetic duties by unit in the different S1 tested scenarios.

Stage	Units	O	S
Heater1	kW	165.9	165.9
Cooler1	kW	165.7	165.8
Heater2	kW	62.4	34.8
Cooler2	kW	58.4	34.8
Cooler3	kW	10.9	-
Dist1Con	kW	204.8	-
Dist1Reb	kW	261.3	-

In the case of S2.1, the energetic demand was clearly correlated to the flow treated as initial stream for this section. In general, the process was the same for both precipitated lignin: organosolv and soda. However, the quantity of fed lignin to this section was greater for the soda process and, as a consequence, more material had to be heated. According to the global process, more than 20 % of the energetic duties were required for the organosolv process in comparison with the soda one, which could be considered as the counterpart for the recuperation of the solvent in the case of the organosolv delignification method.

For S2.2, in the case of the organosolv liquor depolymerization process, the reduction of the total energy demand was caused by the removal of the distillation column emplaced in the S1 to recirculate the ethanol used in the organosolv reaction. However, the decrease of the energy demand was not directly correlated with the elimination of this stage because of the greater flow that had to be treated in this new scenario. This fact provoked an increase in the energy consumption in S2.2, specifically more than the double of the consumption generated in S2.1. However, the results

were still lower for S2.2T than in S2.1T, although the reduction was not as high as it was expected (lower than the 10 % in the total energetic duties).

In Figure 6 and Table 6, the distribution of the total energetic demand by unit for the different scenarios proposed for S2 of the flowsheet is detailed.

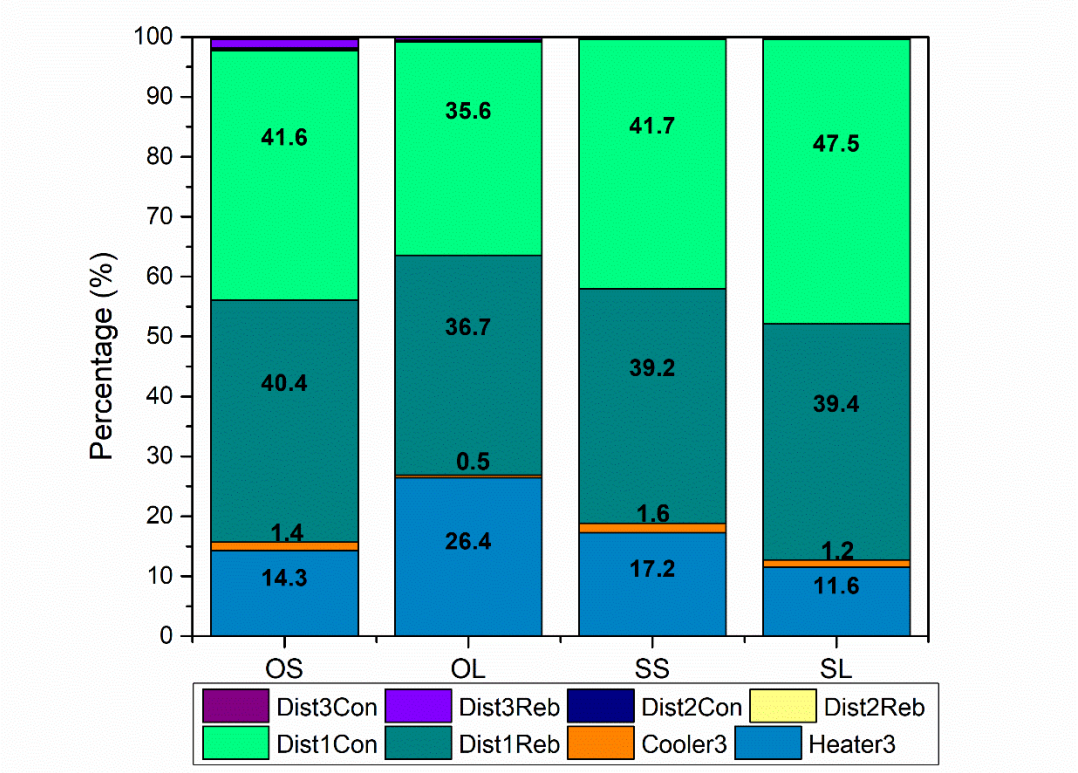

Figure 6. Distribution of energy duties by unit for S2 scenarios.

Table 6. Energy duties by unit in the different S2 tested scenarios.

Equipment	Units	OS	OL	SS	SL
Heater3	(kW)	39.0	144.2	84.8	159.5
Cooler3	(kW)	3.8	2.5	8.0	15.9
Dist2Reb	(kW)	110.7	200.1	192.5	543.8
Dist2Con	(kW)	113.8	194.3	204.9	655.8
Dist3Reb	(kW)	0.8	1.0	0.6	1.8
Dist3Con	(kW)	0.3	0.7	0.4	1.1
Dist4Reb	(kW)	4.3	2.8	0.6	2.0
Dist4Con	(kW)	0.9	0.1	0.0	0.1

Except in the case of the OL simulation, more than the 80 % of the total energetic demand required in S2 was caused by the "Dist2" unit, as sum of its corresponding reboiler ("Reb") and its condenser ("Con"), whereas in the case of the OL was around the 70 %. Despite the maximum temperature that had to be reached in this unit was not relatively high (around 80 ºC), the greater volume to be treated in this stage converted this stage into the most demanding one in terms of energy consumption. Once again, it was demonstrated that the main parameter to be optimized to reduce the energy consumption would be the flows to be treated, trying to reduce as much as possible these huge volumes. The reasons of these high volumes to be treated in the first distillation column of this section was the high volume of ethyl acetate used to extract the phenolic oil from the aqueous stream, resulting after the tar precipitation (5 volumes of ethyl acetate for one of aqueous stream). Therefore, it is thought that, for further cost reductions, this stage should be optimized to minimize the volumes to be handled. The second most important unit in this section was the "Heater3", where the fed stream to the depolymerization reactor was heated until 300 ºC. Establishing a comparison between the different scenarios, it was clear the high impact of the flow to be treated, with greater demands always for the direct liquor depolymerization, where the flows of the reactions were significantly higher. The influence of this stage over the S2 was around 15 % for each scenario, except in the OL, where it represented a 25 %. This fact was based on the greater reduction for the further streams during the flash separations after the depolymerization reaction for the OL scenario, because higher percentages were evaporated when ethanol was used as solvent. From the rest of units, the enormous reduction of the flow caused by "Dist2", minimized the influence of the rest of the distillation columns over the global process. Indeed, the energetic demand of the last two distillation columns could be considered as completely negligible. This was the main reason why such high level of product purification could be afforded; because bearing in mind the whole picture of the global process, a fine separation did not impact on the final production cost in terms of the utilities demand.

3.2.1. Heat integration

The Aspen Energy Analyzer® software did not only report the energetic duties calculated from the simulation developed by the Aspen Plus® software but led to calculate the maximum possibilities to reduce the energy cost using the same flowsheet by energy integration. This is accomplished by combining the existing units through heat exchangers in order to take advantage of their head load. To identify the possibilities that the current flowsheets could present regarding the integration of energy, the methodology of the "pinch" analysis was applied. As first step, the composites curves were built, where temperature vs enthalpy changes are represented. These curves represent the evolution of each stream though its initial and final temperatures. The hot and the cold curves are separated by the selected minimum temperature difference, in this case 10 ºC was the selected gap. Above this point ("pinch" point), heating utilities have

to be applied whereas, below it, cooling utilities have to be applied instead. The composite curves for the four approached cases are presented in Figure 7.

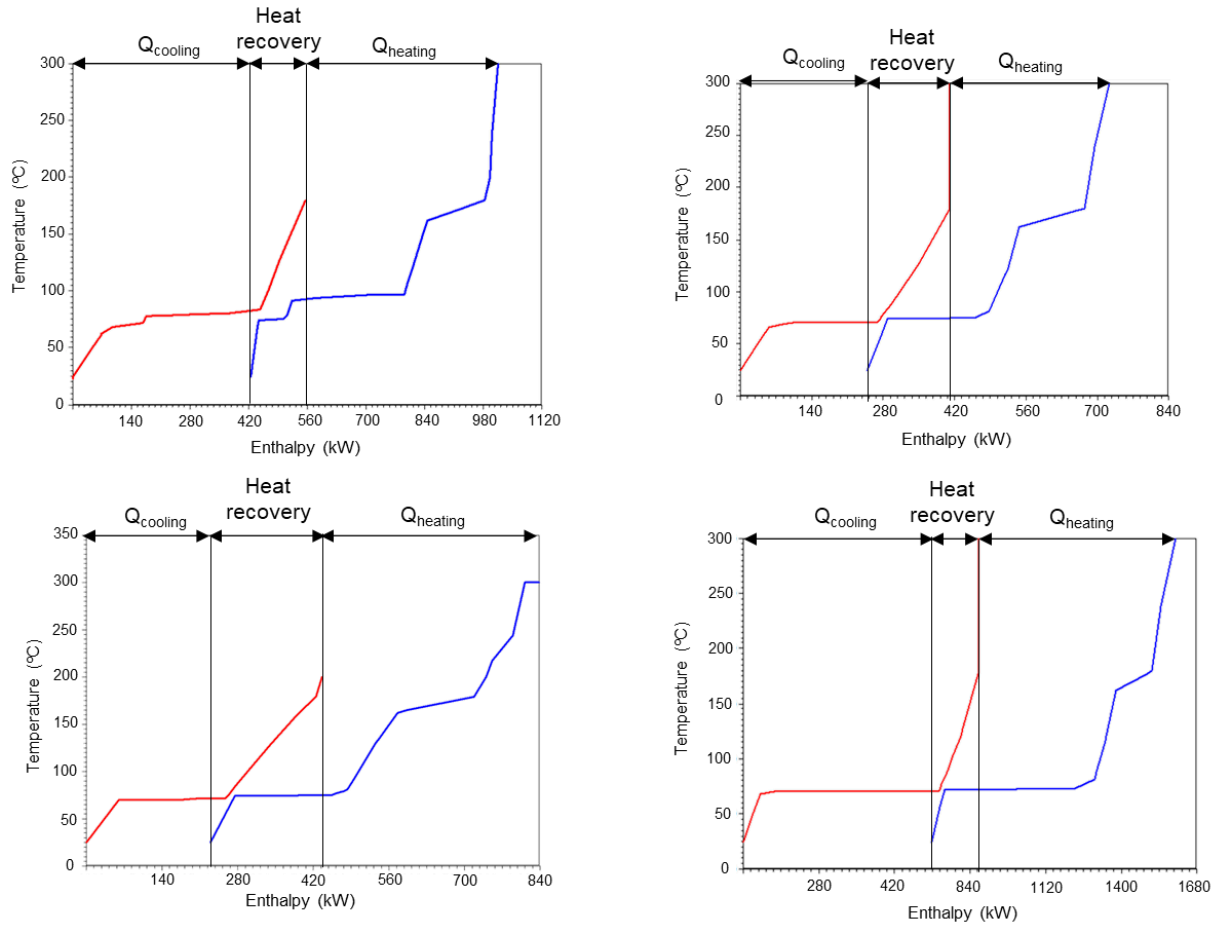

Figure 7. Composite curves of the proposed simulation cases. A) Solid organosolv lignin. B) Liquor organosolv lignin. C) Solid soda lignin. D) Liquor soda liquor

From these curves, the theoretical available energy that could be used by the energy integration was calculated (section from the center of the curve). The theoretical maximum available savings from the base case simulations are detailed in Table 7.

Table 7. Potential savings in energetic duties for global processes.

Parameter	Units	OS	OL	SS	SL
Base Simulation	kW	1,140	1,040	879.2	1,767
Target Simulation	kW	880.5	629.7	558.1	1,419
Potential Saving	%	22.8	39.5	36.5	19.7

In the case of the solid lignin depolymerization, SS allowed higher percentage of energy integration (almost a 40 %). However, the absolute value was bigger for the organosolv process as the energetic duties in the base case simulation were noticeably higher for the latter one. Considering the four global scenarios when lignin was depolymerized from solid samples, the SS scenario presented more possibilities to achieve higher energy savings in percentage and absolute value. Regarding the processes that used liquor as feedstock for the lignin depolymerization, the OL process

showed bigger potential of energy savings in absolute values as well as the total percentage. This fact adds even more negative vision of the direct depolymerization in the soda process as it was not only the process with the highest energy demand, but also the integration possibilities are not at the level of the rest of the tested scenarios.

3.3. Economic assessment

The first step to carry out the economic evaluation was the sizing calculation to estimate the cost of the equipment needed in each scenario. The costs per group of equipment are detailed in Table 8.

Table 8. Purchased and installation costs (BMC) of the equipment needed in each scenario.

Equipment	Units	OS	OL	SS	SL
Heat Exchangers	k€	1,877	3,519.5	3,722	5,138
Reactors	k€	1,302	1,625.1	1,437	1,907
Distillation Columns	k€	1,415	749.1	752.0	1,573
Absorption Column	k€	518.1	818.1	825.1	1,709
Separator units	k€	1,089	952.5	1,174	1,455
Tanks	k€	877.9	231.7	439.4	43.6
Total BMC	**k€**	**7,078**	**7,896**	**8,350**	**11,826**

Based on these estimated results it can be established that the investment for equipment would be lower for organosolv process with lignin precipitation prior to its depolymerization. The higher cost of soda processes with regard to organosolv ones was caused by the higher flows that had to be handled in these processes. The greater lignin extraction yield in soda process involved much more NaOH to be used to dissolve lignin before its depolymerization, and subsequently it increased the volume of ethyl acetate needed to separate the phenolic oil from the aqueous phase. As a consequence of the greater flows to be treated, the size of the equipment units was noticeably bigger in the soda process, making this process much more expensive (almost 20 % more cost). The same situation was undergone when direct lignin depolymerization from the liquors was approached. Not isolating lignin prior to its depolymerization involved an increase of the volume that had to be driven to 300 ºC and 90 bars at the depolymerization reactor. This means that the most expensive stage in the whole process significantly increased by the accretion of more volume to be treated. In case of the organosolv process, the avoiding of lignin precipitation stage led to an increase in equipment cost of more than 10 %, whereas in soda process the increase to avoid that stage was more than 40 % only in equipment. This fact highlights the great sensitivity of the process regarding the solvent ratio used in the depolymerization reaction. As it can be seen, the bigger increment in BMC costs with regard to OS simulation were located on heat exchangers units because energetic duties for depolymerization reaction had to be applied by a direct furnace equipment, a unit much more expensive than a common heat exchanger. There were also differences in reactor costs based on the higher volumes they had to be treated in rest of simulations. In addition, the bigger cost for distillation column in OS process for the ethanol recovery stage was buffered for the previously mentioned over costs, thus the inclusion of the distillation column did not involve a direct increase in equipment costs.

Hereafter, the estimations of the operational costs were calculated based on the utilities, raw materials, labors, and waste treatment costs. The cost breakdown for utilities and raw materials are detailed in Table 9 and Table 10.

Table 9. Utilities costs breakdown by stream.

Stream	Units	OS	OL	SS	SL
Cooling	k€	3.0	2.3	2.2	4.7
LP Steam	k€	38.2	23.4	22.5	63.6
MP Steam	k€	0.0	0.0	4.3	3.8
HP Steam	k€	32.4	34.8	23.7	23.7
Furnace heat	k€	14.2	60.6	30.2	57.1
Total utilities cost	**k€**	**87.8**	**121.1**	**82.9**	**152.9**

At first, it has to be mentioned that the cost of the cooling stream was almost negligible based on the current low cost of water that was considered as a reference (a paper industry in the region in which this work was proposed – the Basque Country). Consequently, the utilities costs were significantly reduced. Therefore, the total final costs of the utilities were mostly generated by the heating streams. Once again, the main differentiation in the cost amongst the proposed simulations was created by the energetic duties of the depolymerization stage where it was compulsory to use a furnace to reach the reaction temperature. The higher energetic duties for the direct depolymerization were caused by the bigger volume to be warmed up in this stage. This was the reason why the OL and the SL simulations presented the bigger costs. Comparing the solid lignin depolymerization simulations, the utilities costs were lower for the SS scenario despite the bigger cost in the depolymerization stage. The inclusion of the distillation column in the S1 in the OS simulation to recover the ethanol provoked this higher cost.

Table 10. Raw materials costs breakdown for the different developed simulation processes.

Stream	Units	OS	OL	SS	SL
Biomass	k€	344.1	344.1	344.1	344.1
Ethanol	k€	38,066	637,727	0.0	0.0
NaOH	k€	8,929	0.0	60,708	41,214
Acid	k€	14,591	0.0	40,735	140,290
Ethyl Acetate	k€	18,865	30,297	22,716	59,124
Water	k€	353.8	258,321	94.5	94.5
Total	**k€**	**81,148**	**926,689**	**124,598**	**241,067**

The raw material costs also drove to identify great differences between the simulation processes as the total costs hugely varied from one simulation to other. OS scenario was the cheapest scenario based on the recovery of the solvent (mixture of ethanol/water) after the delignification stage. As the compounds with the highest costs were ethanol and ethyl acetate, the reduction of the required volume from these streams led to a significant reduction in the cost in comparison with other simulations. Specifically, with regard of the OL simulation, the non-recovery stage of the ethanol in the S1 for the OL scenario deeply increased the final cost of the raw materials in more than 10 times. In addition, as it was observed before, the insertion of the distillation column for the first scenario did not mean an increment of the equipment costs and only the energetic requirement was increased, but in an acceptable level. In the case of the soda processes, the impossibility to recover the solvent after the delignification stage provoked an increase in the costs of consumed chemicals with high costs for both alkaline and acids streams. Only in the SS scenario, the raw material cost was increased by around 50 % in comparison with the OS one. The cost for the SL scenario was almost double than the SS process as a consequence of the greater volume that was driven to the S2, which led to a relevant escalation in the acid and ethyl acetate expenditures to precipitate the tar and to extract the phenolic oil.

From the previous sizing and operational calculated costs, the summary of the total project is described in Table 11.

Table 11. Economic evaluation for the studied processes.

Parameter	Units	OS	OL	SS	SL
BMC	k€	7,078	7,896	8,350	11,825
FCI	**k€**	**16,678**	**18,605**	**19,675**	**27,864**
C_{OL}	k€	936.0	861.4	861.4	861.4
C_{UT}	k€	87.82	121.1	82.91	152.9
C_{WT}	k€	49.79	46.53	56.35	48.83
C_{RM}	k€	81.15	926.7	172.1	241.1
COM	**k€**	**7,494**	**8,907**	**8,244**	**10,698**

In line with the previous values, the OS scenario obtained the lowest FCI cost, which identified this process as the cheapest scenario to initially invest. In addition, the total operational costs (COM) were also lower than the rest of the approached scenarios. These facts highlighted the greatest efficiency of the OS process over the rest of the tested simulation processes. Concretely, the total FCI cost was increased in more than 10 % for the OL simulation and the COM cost in almost 20 % for the OL simulation, mostly based on the higher reactant costs. However, this process was behind the direct lignin depolymerization processes (OL and SL ones) in terms of the phenolic monomers production, which it is thought to have an important influence in the case of a great final price for this stream. It has to be reminded that the volume of this product was really low in comparison of the fed biomass. The soda processes were more expensive than the organosolv processes in terms of the FCI costs, being bigger for the direct depolymerization from the liquor, as well as in the organosolv processes. As it was commented before, the greater volume in the critical stages that had to be handled in these processes led to such increase in the investment costs. The same situation was experienced with the COM costs. In this case, it was caused by the high demand of chemicals that the soda processes required.

4. Discussion

The current commercial price of the obtained products included in the Supplementary data (see Table S7), was used to calculate the revenues (Supplementary data, Table S8). A negative economic balance was obtained even for the most beneficial scenario (OS), which was identified in previous analysis. These results are in line with the results reported by other authors, such as Chrisandina et al. (2019), who studied the precipitation of lignin prior to the pulping process and obtained a cost of the process higher than the estimated commercial price (0.3 $/kg). It was a more realistic price that the used by other authors, whose economic performance was reported to be better. Even considering higher price of the products, with a lignin price of 630 €/t, still the economic balance was negative for their simulated integrated biorefinery (Nitzsche et al. 2016). Shen et al., (2019) reported a not economically feasible scenario to valorize lignin as jet-fuel as well. However, the results shown in these works highlight the promising character of these approaches and establish the further steps necessary for reaching desirable scenarios. On the other hand, other works already reported promising results, with positive economic results (Moncada et al., 2018). However, the balance presented was very sensitive to the price of the product, which was fixed at very high value (lignin price of 630 €/t). A brief economic analysis about the lignin depolymerization stage developed by Mabrouk et al., (2018) demonstrated that the catechol production could be economically feasible, as the price needed to recover the initial investment was inside the range of current commercial prices. This result indicates that lignin depolymerization process would be a very promising way to enhance the profitability of a biorefinery facility.

5. Conclusions

The different scenarios evaluated in this work by simulation processes were assessed in terms of product yields, raw material consumption and waste streams disposal. From the first section of the tested processes, soda delignification method had the greatest lignin yield (around 100 % more). However, pulp yield, another interesting product to be considered in a fully integrated biorefinery approach was poorer than in organosolv process. The most significant difference between both processes was the possibility to recover the solvent from the delignification stage in organosolv process, which reduced the consumption of chemicals almost to a negligible degree.

Considering the second section of the process, where lignin was depolymerized including a previous precipitation stage or it was directly depolymerized from the liquor, it was confirmed that regardless the higher lignin amount extracted in soda process, organosolv lignin was more suitable to be depolymerized, leading to greater phenolic monomers yield than in soda processes. It was also demonstrated that the direct depolymerization kept or enhanced the product yields.

In addition to the mass balances, energetic and economic assessment were accomplished. By the energetic analysis, it was established that the great impact caused in OS simulation by the inclusion of ethanol recovery distillation column was buffered by the reduction of the treated volume in Section 2, were the most critical stage in terms of harsh conditions was located (depolymerization reaction). This is also the reason why the energetic demand for SL scenario was really high, as the flow treated in this stage was much bigger than in other simulations. However, the SS simulation was the flowsheet with the minimum energetic demand.

Besides the traditional energy assessment, a “pinch” analysis was carried out to identify potential energetic savings in the process in order to approach optimized simulations in further investigations. In this sense, great possibilities to reduce utilities demand were found for all proposed flowsheets with OL scenario presenting almost 40 % of utilities reduction.

Finally, economic analysis was conducted following the Guthrie’s method to calculate both FCI and COM parameters. FCI and COM costs were extremely influenced by the high volume to be treated at the most critical stage, specifically the lignin depolymerization reaction where harsh conditions (temperature and pressure) were required. As a consequence, the cost of the equipment to supply such energetic duty and withstanding those conditions were deeply incremented. Therefore, in order to reduce the cost for further investigation two alternatives could be proposed: (i) reducing the liquid/solid ratio for every reaction of the circuit, especially for depolymerization reaction, and/or (ii) reducing the harsh conditions of the depolymerization stage to be capable to use more economically feasible equipment. In any case, in both alternative reaction yields are expected to be negatively modified, mainly in the second alternative.

Calculation of revenues was difficult to be addressed due to the generation of different product streams (catechol derivatives, phenolic oil, unbleached pulp, and tar streams). However, using current commercial prices for these streams the profit and loss accounts were negative for all tested cases. In this sense, it was demonstrated the negative influence of the oversized flows handled in some stages on the final cost of the processes, both in investment as well as in operational costs. In any case, the economic evaluation has been important to identify which simulation process presented the best conditions. OS was demonstrated to be the most feasible solution in these conditions since its cost in FCI and COM were the lowest of the four different scenarios tested. Uniquely, it has to be considered the greater yield in catechol derivatives for direct depolymerization processes from the liquors (OL and SL).

Acknowledgements

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