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A Study of Organosolv Ethanol-based Processes for the Selective Fractionation of Relevant Agroforest Residues

Filipa Pires* , Florbela Carvalheiro[a], José Granjo[b]

[a] *LNEG – Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia e Biorrefinarias, Estrada do Paço do Lumiar, 22, 1649-038 Lisbon, Portugal*

[b]*CERENA, DEQ, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001, Lisbon, Portugal*

ABSTRACT

In this work, an organosolv approach based on ethanol/water mixtures was studied for two model lignocellulosic feedstocks, one from agriculture origin (wheat straw, WS) and another from forest origin (*Eucalyptus globulus* residues, ER). The process conditions were studied aiming at an integrated biomass upgrade concept that selectively remove and depolymerise lignin and hemicellulose, producing lignin-derived compounds and soluble oligo- and monosaccharides, as well as an easily digestible polysaccharide (mainly cellulose) containing solid.

In a first approach, non-catalysed organosolv pre-treatments were conducted using ethanol/water mixtures (50:50) at 190ºC and reaction times ranging from 0-120 min. The 120 min treatments proved to be the most efficient for both residues with relatively high delignification yields (59% and 70.9% for WS and ER, respectively). The cellulose-rich solids undergo enzymatic hydrolysis achieving for WS and ER 68.5% and 71.7% of enzymatic digestibility yields, respectively. Non-catalysed organosolv pre-treatments at 190ºC were more efficient for ER than for WS. Thus, ethanol/water organosolv treatments at milder temperature (140ºC) and low catalyst concentration (12-50 mM H_2SO_4) were optimised, using a statistical experimental design, following a Doehlert distribution. The highest delignification yields and enzymatic digestibility, 86.4% and 84.1%, were obtained for 25mM sulfuric acid concentration and 90 min reaction time. A simulation using Aspen Plus® software was conducted to perform a data reconciliation analysis followed by process optimisation using heat and mass integration. Pinch analysis was made to predict potential energy savings.

Keywords: biorefinery; ethanol organosolv; eucalyptus residues; hemicellulosic sugars; lignin; wheat straw

1. Introduction

The growing need for alternatives to fossil fuels, the most used resource in chemical industries for decades and the cause of many environmental concerns, has led to the research for greener alternatives. In an attempt to solve these problems, biomass, as a sustainable resource, has been studied. Bio-waste (estimated at up to 138 million tons per year in the EU, of which up to 40 % is land-filled) has high potential added value as a feedstock for other productive processes [Horizon, 2020]. Agroforestry residues, as wheat straw and eucalyptus residues are generally seen as undesirable

* *Corresponding author.* Tel.: +351 916 097 682;
E-mail address: filipa.pires@tecnico.ulisboa.pt

by-products, resulting in high costs in their treatment and their use commonly consist of low-value applications. However, lignocellulosic materials should be faced as an opportunity, as they are a realistic option for the production of biofuels and other products with great potential and added value. Thus, the transformation of this type of waste, efficiently and in a context of biorefineries can bring several benefits. The bio-refining industries will have the capacity to evolve, stimulating the local economy and revitalising rural areas.

Organosolv pretreatments are increasingly studied for such purposes. These delignification processes are among the most promising options for industrial implementation since they may enable an integrated fractionation of biomass and benefit from a lower CAPEX, specifically if ethanol is the based solvent.

In this work, an organosolv approach based on ethanol/water mixtures with or without catalyst was studied. The process conditions were studied aiming at an integrated biomass upgrade concept that selectively remove and depolymerise lignin and hemicellulose, producing lignin-derived compounds and soluble oligo- and monosaccharides, as well as an easily digestible polysaccharide (mainly cellulose) containing solid.

2. Materials and methods

2.1 Raw material

Two lignocellulosic materials were used as feedstocks in this work: wheat straw (WS) and wood residues from Eucalyptus globulus (ER). The WS residues were purchased in Germany and kindly provided by ECN-TNO (Netherlands). This material was previously milled to particles < 4 mm. The eucalyptus residues, a by-product from wood chips production, were kindly provided by The Navigator Company (Cacia, Portugal). This feedstock was not milled, and it was used "as it is".

Both feedstocks were stored in card boxes at room temperature until use and its chemical composition is shown in Table 2.

2.2 Organosolv fractionation

2.2.1. Wheat straw and eucalyptus residues fractionation under non-catalysed conditions

Organosolv experiments were conducted at laboratory scale in a(600 mL) stirred Parr reactor (Parr, USA) using ethanol/water mixtures of 50% (w/w) and a liquid-to-solid ratio (LSR) of 10:1. For the first trials (no-catalyst added) and for both feedstocks, the temperature was set at 190ºC and the reaction time ranged from 0-120 min.

After reaction time was over, the reactor is rapidly cooled by water circulating through a serpentine coil, and the solid and liquid phases were separated by pressing using a manual press. The resulting liquid was weighted, filtrated under vacuum (Whatman filter paper no. 1), weighted again and stored at 4 °C for future analysis.

The solid phase was washed twice with the amount of the ethanol/water solution used in the organosolv process, followed by the double amount of water at 70 ºC. After, the solid residue was dried at 45 °C for at least 48 h before chemical characterisation.

2.2.2. Organosolv fractionation of eucalyptus residues under catalysed conditions - Doehlert statistical experimental design

For ER, ten assays, including four replicates at the centre of the experimental domain, were done according to a Doehlert statistical distribution for two factors [Doehlert, 1970]. The temperature was set at 140 ºC and sulphuric acid concentration (X1) and time (X2) were the two factors studied in an experimental domain that ranged from 0-50 mM and 0-180 min, respectively. Table 1 shows the number and conditions in which the assays were conducted. The organosolv process occurred as described in Section 2.2.1.

The model used to express the responses was a second-order polynomial equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \quad (1)$$

β_0 is the regression coefficient at centre point; β_1 and β_2 are the linear coefficients of variables 1 and 2, respectively; β_{12} is the second-order interaction coefficient between variables 1 and 2; and β_{11} and β_{22} are the quadratic coefficients for variables 1 and 2. The linear multi-variable regression to equation 2 and its analysis of variance (ANOVA) was carried out using Microsoft® Excel 2018 Regression tool pack, using all replicates.

Table 1. Factors values in coded units and real units for the statistical planning assays.

Experiment	Coded units		Real Units	
	H_2SO_4 (X_1)	Time (X_2)	H_2SO_4 (mM) (U_1)	Time (min) (U_2)
1	0	0	25	90
2	1	0	50	90
3	-1	0	0	90
4	0.5	0.866	37.5	167.94
5	-0.5	-0.866	12.5	12.06
6	0.5	-0.866	37.5	12.06
7	-0.5	0.866	12.5	167.94
8	0	0	25	90
9	0	0	25	90
10	0	0	25	90

The best conditions for hydrolysis were found using the Microsoft Excel® 2018 Solver tool based on the best-fit equations using a constrained model.

2.3 Analytical methods

2.3.1 Quantification of monomeric sugars, oligomeric sugars, and degradation products

Quantification of oligosaccharides (OS) was performed by an indirect method based on the post-hydrolysis of liquors according to NREL/TP-510-42623 protocol (Sluiter et al., 2012). This method consists in the addition of concentrated sulphuric acid (72% (w/w)) to the liquors from the organosolv treatments to achieve a final H_2SO_4 concentration of 4% (w/w). The mixture was placed in an autoclave for hydrolysis (60 min at 121 ºC). After the autoclave cycle was over, the hydrolysates were cooled down to room temperature. Afterwards, a sample was taken and filtered through 0.22 µm membranes (Millipore®) and analysed by HPLC. at 50 ◦C with 5 mmol/L H_2SO_4 at a flow rate of 0.6 mL/min. Glucose, xylose, arabinose and acetic acid were detected with the RI detector, while furfural and HMF were detected with the UV detector at280 nm. Thus, the concentration of OS present in the samples, which were calculated considering the increase in sugar monomers in relation to the initial values. All assays were conducted in duplicate.

2.3.2 Quantification of polysaccharides, acetyl groups and Klason lignin

The feedstocks and pre-treated solids obtained from organosolv treatments were subjected to a quantitative acid hydrolysis according to a method based on NREL/TP-510-42618 protocol (Sluiter et al., 2011) to determine polysaccharides content (glucan, xylan, arabinan), acetyl groups and Klason lignin.

This method consists in the addition 5 ml of sulfuric acid (72% w/w) to 0.5 g of a solid sample. Afterwards, the test tubes were immersed in a Memmert (Schwabach, Germany) W350 water bath for 1 h at 30 ºC, with occasional manual stirring. Next, the content of the tubes was transferred to 250 ml Schott flasks and water was added to reach an H_2SO_4 concentration of 4% (w/w). The samples were then autoclaved at 121 ºC for 1 h. After the reaction time was over, the flasks were cooled down, and the mixture was filtered through sintered glass crucibles (#3 porosity) previously incinerated in a muffle furnace. Klason lignin corresponds to the solid remaining in the crucibles, washed with 100 mL of distilled water, dried in an oven at 100 ºC until constant weight and then burned in a muffle furnace for correction for ash content. A sample of the liquid phase obtained was analysed by HPLC for quantification of sugars, acetyl groups and acid-soluble lignin. The procedure was performed in duplicate for each sample.

2.3.4 Enzymatic hydrolysis

The enzymatic hydrolysis method was carried out in duplicate and performed in both pre-treated solids and raw materials. To initiate the procedure, 0.5 g

of biomass were weighted (in 40 ml capped plastic tubes). Water was added followed by a solution of 5 mL of a sodium citrate buffer solution (pH 4.8) and 100 µL solution of sodium azide to adjust the volume to 10 mL, considering that the biomass density was 1. Samples were autoclaved at 120 ºC for 10 min and, after cooling, 10% of a commercial enzyme complex, Cellic® CTec2 (g enzyme/100 g cellulose) (activity 199.9 FPU/ml), kindly provided by Novozymes (Denmark) was added.

Two blank assays were also prepared in each series of tests. In one blank, to assess the presence of glucose oligomers, no enzyme was added to the substrate, while on the other blank the enzyme was added without a substrate to determine the amount of glucose present in the enzyme.

Samples were incubated (180 rpm) at 50 ºC for 72 h. Once the incubation period was over, the enzyme was deactivated by incubation in a water bath at 100 ºC for 10 min. Finally, the samples were filtered under vacuum conditions through Millipore® membranes (0.45 µm) followed by 0.22 µm syringe filters before HPLC analysis.

2.3.5 Process simulation and analysis

Organosolv pretreatment was modelled and simulated in Aspen Plus®. Here, it is analysed the pretreatment process of Eucalyptus residues with non-catalytic organosolv at 190 ºC and 120 min (isothermal period). The flowsheet structure is similar to others reported in the literature (Kautto et al., 2013). The process modelling and simulation approach is similar to previous works (Granjo, 2017).

It was considered a plant operating continuously 7977 hours per year (91% of stream factor) and a biomass processing capacity of 100 ktonne/y (12,500 kg/h). The feed consists of previously prepared eucalyptus residues, which, to improve delignification and hydrolysis, are impregnated with high-pressure live steam during the pulping. The temperature of the impregnated residues is raised to the pulping temperature through the amount of injected live steam.

3. Results and discussion

3.1. Chemical Characterisation

According to the protocols described previously, to assess the content in these main macromolecular constituents and ash and other extracts, a chemical characterisation of the biomasses was carried out. Table 2 presents the results obtained.

Both materials present a polysaccharide content of approximately 63%, with cellulose being higher than hemicellulose. It is important to note that ER present lignin quantities, close to 30%. This evidence shows the great potential for valorisation that both materials have.

Table 2. Average chemical composition (dry basis) of WS and ER.

	WS	ER
Celullose	36.6	44.5
Hemicellulose	26.4	18.5
Xylan	20.8	15.2
Arabinan	2.1	0.5
Acetyl groups	3.5	2.8
Klason lignin	15.7	26.4
Acid soluble lignin	1.7	7.7
Ash	11.4	1.8
Others(by difference)	8.2	1.1

3.2 Non-catalysed organosolv fractionation

Being organosolv a delignification method, the lignin removal (i.e., delignification yield) and the amount of lignin recovered are parameters to consider and one of the most interesting discussion points. For the WS treatment without the isothermal phase (0 min), the lignin remaining in the solid is 80.2%. Thus, the heating phase until 190 ºC contributes to a 19.8% delignification of the material (Figure 1a). The treatment with an isothermal phase of 120 min appears to be the most effective, with a delignification yield of 59%. For ER (Figure 2a), the highest delignification was also obtained for 120 min treatment. Under these conditions, the Klason lignin percentage remaining in the solid (29.74%), corresponds to a 70.3% delignification yield. The less severe treatment (0 min) presents a delignification yield of 26.1% with 73.9% of lignin still present in the solid. Besides delignification,

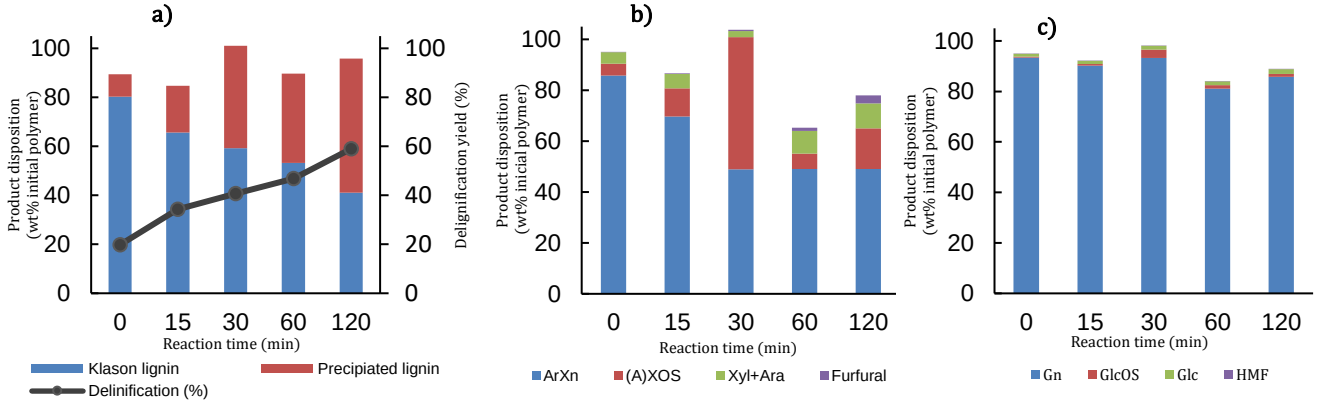

Figure 1. Product distribution for WS ethanol based organosolv fractionation at 190ºC as a function of the isothermal reaction time (no catalyst added).

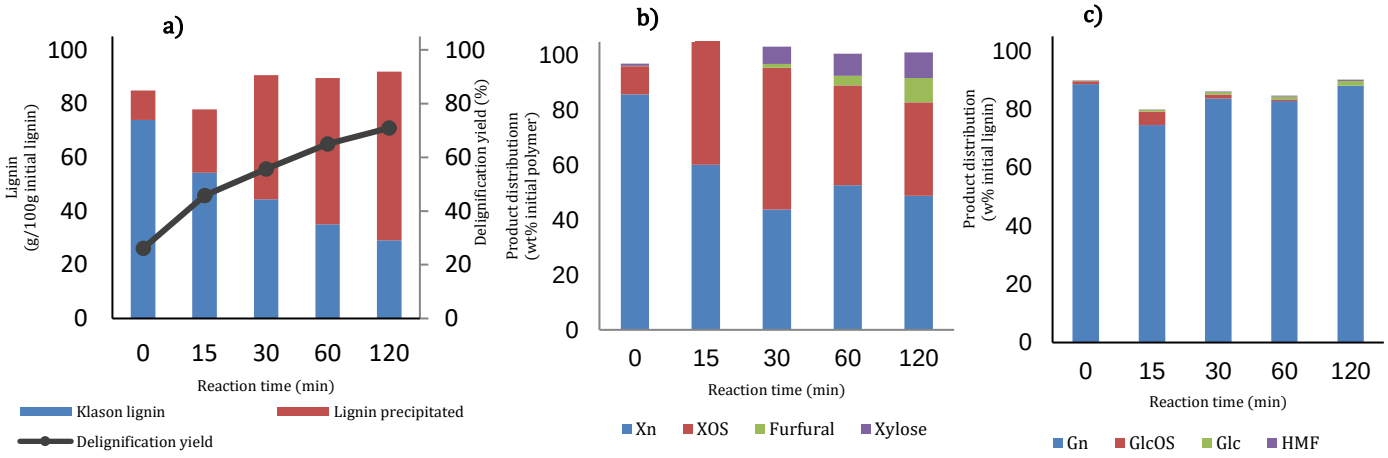

Figure 2. Product distribution for ER ethanol based organosolv fraction at 190 ºC as a function of the isothermal reaction time (no catalyst added).

these organosolv treatments also lead to a partial hydrolysis of hemicellulose and xylan solubilisation, which increases to reach values around 50% for both feedstocks, although slightly higher for ER (Figures 1b and 2b).

The formation of xylo-oligosaccharides (XOS) and xylo-oligosaccharides substituted with arabynosil residues (A)XOS, in ER and WS respectively, have their respective higher values (close to 50% of the recovered hemicellulosic sugars) at 30 min. For the 2 h treatment (A)XOS reach a final composition of 15 and 34.1 g/100g initial xylan for WS and ER, respectively. The monomeric pentoses in WS present its higher concentration value at 2 h with 9.9 g/100g xylan, while its lowest at 30 min with 2.41 g/100g initial component. In ER, the best treatment conditions for xylan hydrolysis are 120 min, with a xylose concentration of 9.4 g/100g initial xylan. The decrease of xylose and arabinose is mainly due to their degradation, generating an increase of furfural concentration associated with the increase of process severity, reaching its higher values for the 2h treatments for both materials. Even though xylose slightly increases in the ER 2h treatment, there is still a considerable furfural formation compared with the shorter reaction time treatments.

Cellulose, measured as glucan, was practically not degraded (Figures 1c and 2c) by organosolv treatments, remaining mainly in the solid phase (85.8% of the initial cellulose for WS and 88.1% for ER for the 2 h reaction time). Even though some solubilisation occurs and there is also the formation of glucose oligomers (gluco-oligosaccharides, GlcOS) that presents its maximum values, 3.3 g/100g glucan (30 min assay) and 4.58 g/100g initial glucan for WS and ER, respectively. Hydroxymethylfurfural (HMF) results from degradation reactions of glucose, that is boosted

by the increase of process severity. Thus, this degradation product attains higher values for the 2h treatments, which are considerably more visible in the ER. Comparing both residues, eucalyptus exhibited both higher xylan solubilisation and delignification, making ER a more efficient feedstock to be used in a non-catalysed organosolv process. As no acid was added, the behaviour observed can be related to a higher buffer capacity of WS as compared to ER and which can be related to the higher ash content found for WS.

3.3 Enzymatic Hydrolysis of pre-treated solids

The efficiency of ethanol-based pre-treatment on WS and ER was also evaluated by enzymatic hydrolysis. The saccharification yields of pre-treated WS and ER were performed as described in section 2.3.4, using an enzyme dose of 10% based on pulp glucan. The results obtained are shown in Figure 3.

At 190°C with no catalyst added, enzymatic cellulose conversion to glucose increases with pre-treatment time to reach the highest values for 2 h reaction, respectively 68.5% for WS and 71.7% for ER. These values represent near to 5-fold and 7-fold increase compared to the original feedstocks, i.e., 10.6% and 14.2% for WS and ER, respectively. According to Wilschut et al. (2013), the enzymatic digestibility (using Accellerase 1500 as cellulase) achieved was about 42% for wheat straw using 50% ethanol/water at 190 ºC and 120 min, a much lower value than the one found in this

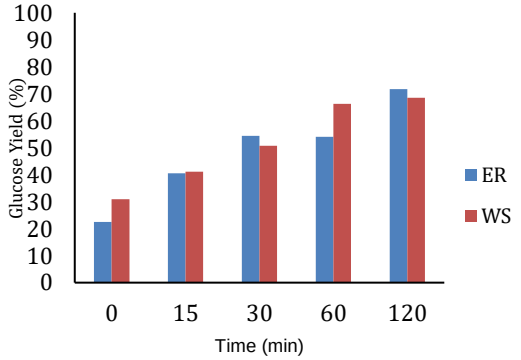

Figure 3. Enzymatic saccharification of ethanol:water organosolv pulp for WS and ER obtained at 190ºC without catalyst addition.

work. Wang et al. (2017) used Eucalyptus wood in an organosolv process with 50% 2-Propanol/water for 2 h at 200ºC, and obtained an enzymatic hydrolysis glucose yield of 80.05%, a higher value than the one found in this work, however with a different solvent.

All in all, eucalyptus residues seem to be slightly efficient biomass out of the two in the study in this thesis, with higher delignification and saccharification yields for the 2 h treatment, as well as high xylose solubilisation and XOS formation when compared to wheat straw 2 h assay.

3.4 Acid catalysed organosolv fractionation – Doehlert experimental design

As eucalyptus was the biomass with the most promising results from the presented autocatalysed organosolv processes, these residues were submitted to a catalysed organosolv process following a Doehlert experimental design for two factors to maximise both sugars and delignification yields and establish optimum conditions [Doehlrt,.1970].

Several preliminary experiments were carried out at mild temperature (140 ºC) with and without catalyst (sulfuric acid) to fix the reaction temperature.

The traditional 'one-factor at a time' technique that can be used to optimise a multi-variable system is not only time-consuming but also often misses the alternative effects between components. In addition, this method requires to carry out several experiments to determine the optimum levels, which are untrue. These disadvantages associated to the single factor optimisation process can be eliminated by optimising all the affecting parameters collectively by Doehlert experimental design using response surface methodology (RSM).

RSM is a sequential procedure which has an initial objective of leading the experimenter rapidly and efficiently to the general vicinity of the optimum. Since the optimum location is unknown prior to running RSM experiments, a design that provides equal precision of estimation in all directions is employed. The base points for the design were selected from the single parameter study. The second-order polynomial equation was found by applying multi-variable regression analysis on the experimental data (equation 1).

Table 3. Parameter values for the quadratic polynomial equation.

Yield (%)	β_0	β_1	β_2	β_{12}	β_{11}	β_{22}	R^2
Delignification	**82.6±5.4 (0)**	**29.2±6.3 (0.010)**	7.6±6.3 (0.290)	-16.8±12.5 (0.251)	**-35.6±9.4 (0.019)**	-11.1±9.4 (0.303)	**0.91**
Xylose	**63.3±2.9 (0)**	**23.9±3.3 (0.002)**	**8.9±3.3 (0.050)**	-4.2±6.7 (0.559)	**-34.6±5.0 (0.002)**	-13.7±5.0 (0.052)	**0.97**
Glucan Recovery	**92.6±0.6 (0)**	**-3.3±0.7 (0.009)**	**-2.9±0.7 (0.014)**	-0.9±1.4 (0.558)	1.6±1.0 (0.199)	2.8±1.04 (0.060)	**0.93**
Saccharification	**81.7±6.0 (0)**	**29.7±6.9 (0.013)**	**19.6±6.9 (0.046)**	-24.0±13.8 (0.156)	**-36.9±10.3 (0.023)**	-22.3±10.3 (0.097)	**0.92**

*Coefficient ± standard error. **Statistically significant ($p < 0.05$) coefficients are bold**

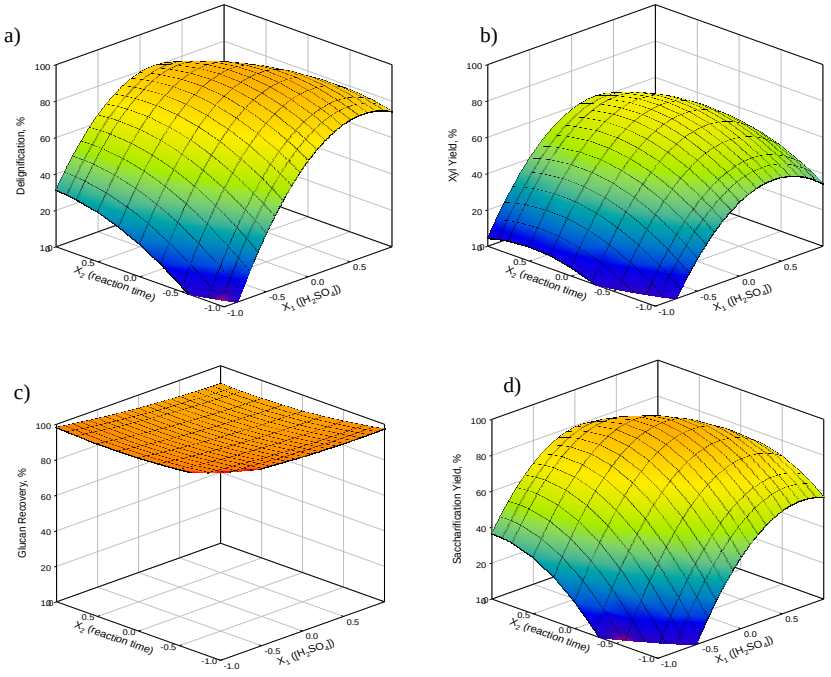

Figure 4. Response surfaces for the most relevant parameters.a) Delignification; b) Xylose yield; c)Glucan recovery, d)Saccharafication

The RSM results are given in Table 3 and Figure 4 for delignification, xylan yield, glucan recovery, and saccharification. The significance of each coefficient was determined by p-values. The smaller the magnitude of the p-value, the more significant is the corresponding coefficient. By the analysis of both Table 3 and Figure 4ait is possible to see that delignification is influenced by catalyst concentration in a way that low concentrations have a positive effect while higher concentrations induce a detrimental one. As stated, the higher delignification yield achieved for this set of experiments, was 86.7% for conditions close to the centre of the experimental domain (90 min and 25 mM H_2SO_4).

The xylose production yield is both influenced by reaction time and catalyst concentration. It is positively affected by low H_2SO_4 concentrations and to a less extent by reaction time. In addition, a negative effect exists for high catalyst concentration, thus inducing the production of sugar degradation products like furfural.

Glucan once more presents high values in the pulp, regardless of the operational conditions (Figure 4c), thus enabling to obtain pre-treated biomass with an extremely high glucan content, with values above 90%

for the optimal conditions. However, as it can be seen and proved by p-values, glucan recovery is still negatively affected (in a small extent) by both catalyst concentration and reaction time.

This rich glucan pulp obtained was subjected to enzymatic hydrolysis, and the saccharification yields obtained are shown (Figure 4d). The saccharification yield is positively influenced by both catalyst concentration and reaction time, although higher catalyst concentrations induce a negative effect on the parameter. The higher saccharification yields (>84%) were found for the conditions close to the center of the experimental domain, with moderate catalyst concentrations.

The statistical data provided by the analysis of variance and the coefficient of multiple determination (R^2) showed that, the best fit for xylose yield with a R^2 of 0.91 implies that 91% of the sample variation in the xylose production is attributed to the independent variables. All other regression coefficients for the parameters in the study were also above 0.90 and the same conclusion can be taken.

Although there are several studies for the fractionation of biomass with ethanol-water mixtures and catalysed with sulfuric acid, in general, they explore higher temperatures and catalyst concentrations, so the available bibliography for comparison of results under similar operational conditions is practically non-existent.

The results obtained in this work show that because eucalyptus is a very reactive material and susceptible to hydrolysis, it can be fractionated, by an organosolv process under very mild conditions of temperature and catalyst concentration, with high efficiency.

3.3.2 Process Simulation

To better understand the application of this study, the mass balances for the main compounds were calculated per tonne of feedstock. With the data obtained and considering the market value for the products (XOS, Xyl, Glc and Lignin) a preliminary economic analysis was performed just for products revenue depending on the feedstock used. This economical approach points the uncatalysed eucalyptus organosolv as the process with higher potential revenues, although no equipment, installations, utilities, or other costs were taken into account.

3.3.2.1 Plant model validation

The model for an organosolv pre-treatment was developed and validated to produce xylooligosaccharides, syrups and lignin. A process flowsheet was designed to follow closely the experimental setup used to collect the experimental data for eucalyptus residues at 190 ºC without catalyst, as per indication of the preliminary economic analysis.

In a first approach, energy integration and recirculation were not taken into account. This simulation served has a data reconciliation analysis, to see if the model created fitted the experimental results obtained.

Deviations for the pulp and hydrolysate leaving the digestor were 0.02% and 0.13%, respectively. The lignin also presented good fts with the model. So, it is safe to conclude that this simulation describes well the experimental results.

3.3.3 Process Optimisation

The process was optimised by using the plant model previously validated. The process was redesigned, and the operating conditions manipulated to reduce energy consumptions and obtain the products within specifications. Then, pinch analysis was performed to evaluate potential energy savings. The new process flowsheet shown in Figure 5 now features a double effect distillation system to recover the solvent, an integrated arrangement which has been shown to reduce considerably the energy requirements in diluted aqueous solutions of ethanol. The double effect distillation system was designed as in [Granjo et al., 2020], and the concentrations of ethanol in the distillates were adjusted to match the solvent composition required in the digester and in WASHER1. The operating conditions of the evaporators in the XOS and syrups concentration areas were adjusted to minimize energy consumptions and obtain the products within the specifications. The pulp leaving the saccharification step was partially recycled to increase the overall production of syrups and improve the pulp delignification. In addition, the water streams were redirected to the digester and washing stages to reduce further the need for freshwater and purge streams are included to prevent the accumulation of inhibitors (e.g., HMF, furfural) in the process.

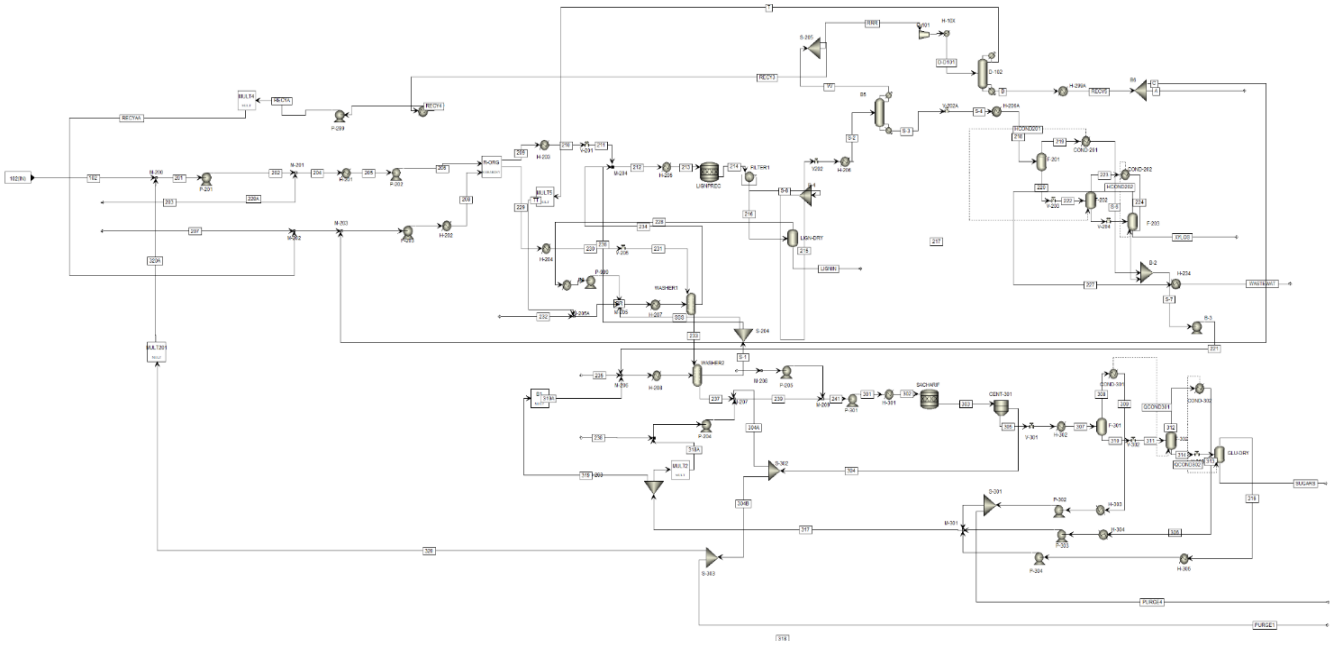

Figure 5. Process optimisation flowsheet.

Table 4. Results of pinch analysis.

Property	*Actual*	*Target*	*Available Savings*	*% of Actual*
Total Utilities (GJ/h)	2045	1152	893.8	43.7
Heating Utilities (GJ/h)	762.3	315,3	447	58.63
Cooling Utilities (GJ/h)	1283	836.2	446.8	34.83
Carbon Emissions (kg-eq/h)	114300	64360	49960	43.7

The results show that the consumption of ethanol and water are greatly reduced with this new process design. A reduction of about 98.4% of ethanol is achieved, from 125328 kg/h to 1964 kg/h. Likewise, freshwater needs are reduced by more than 70%, from 411924 kg/h to 118950 kg/h. By analysing the pinch results, it is clear that energy integration (Table 4) can decrease the overall energy consumption, as the total utilities energy values without integration were about 43.7% higher than the minimum achievable. Both hot and cool utilities attained energy saving in the order of 447 GJ/h, while the overall energy saving in utilities were 839.8 GJ/h. In terms of energy demand per kg of product obtained (C5 and C6 sugars, lignins and XOS), heat integration allow us to reduce down to 20.8 MJ/kg-product. This value compares well with the literature, since Kautto et al. (2013) reports energy consumption of 22 MJ/kg-product for an ethanol organosolv process and Humbird et al. (2011) reports 26 MJ/kg-product with the diluted acid process. Overall, the new design here obtained of the organosolv process has an improved performance not only in terms of energy efficiency, but also with lower environmental impact since carbon emissions attained a value of 6430 kg/h against the previous 114300 kg/h through extensive heat and mass integration.

4. Conclusions

High temperature organosolv pre-treatments (no catalyst added) were more efficient for eucalyptus biomass than for wheat straw. Eucalyptus fractionation proceeds quite faster and almost a complete hydrolysis of hemicellulose occurs at 2h reaction time, with the higher delignification yield (~68%). Significant C5 sugars yields (mainly oligomers, in general) were obtained from the hydrolysis of hemicelluloses. In all

conditions tested, glucan was almost not affected by these treatments, and a low production of C6 sugars is observed yielding solids with a high glucan content. The enzymatic digestibility of the cellulose solid rich attained higher values for the eucalyptus residues than for wheat straw as well. For moderate temperatures and catalyst addiction eucalyptus fractionation also proceeds quite fast. This set of catalysed eucalyptus organosolv experiments were modelled by a quadratic polynomial equation, according to Doehlert experimental design, that enable the definition of the optimal conditions. The higher delignification yields were obtained at the centre of the experimental domain, corresponding to 0.025 M sulfuric acid and 90 min reaction time. The cellulose enzymatic digestibility of the processed solids was assessed and modelled based on hemicellulose and lignin removal. The higher yields were mainly correlated with high delignification yields.

Comparing these data with the non-catalysed process at the same temperature, it is clear that the catalyst plays an important role in the delignification process, as similar results can only be achieved without catalyst if the reaction temperature is considerably higher.

The simulation results were a good fit for the experimental data and the optimisation process allowed to achieve better energy performances as well as reducing its environmental impact.

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