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Study on Soda–Ethanol Delignification of Pine Sawdust for a Biorefinery

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Abstract: The soda–ethanol process was conceived as a sulfur-free pulping process, which may also be an alternative to conventional alkaline pulping, such as kraft or soda–AQ in the biorefinery context. An in-depth study using two experimental designs was conducted to establish the viability of soda–ethanol delignification of pine sawdust. At first, a simple factorial design involving the ethanol–water ratio (ethanol:water) and the alkaline load (*AL*, % over dry wood, odw) was applied to define the levels of these variables and their eventual interaction. Then, a 3^2 experimental design was performed to evaluate the ability of the process concerning the pulping of pine sawdust. The tested conditions were carefully selected to screen a broad range of cooking times (60, 100, and 140 min) and alkaline loads (19.0, 23.3, and 27.6 %odw) to obtain pulps with different extents of delignification (residual lignin contents). Finally, the kraft, soda–AQ, and soda–ethanol treatments were compared. Soda–ethanol pulping was shown to be a suitable delignification stage for a biorefinery scheme of *Pinus elliottii* and *Pinus taeda* sawdust. It has many advantages over traditional processes regarding its environmental impact, harmless chemicals, and selectivity. The tested conditions were similar to those frequently used in conventional pulping at an industrial scale, suggesting the technical feasibility of the soda–ethanol process for pine sawdust processing.

Keywords: pine sawdust; delignification; soda–ethanol pulping; biorefinery

1. Introduction

A forest biorefinery is a structure that can generate fuels, energy, and chemicals from the primary processing of wood lignocellulosic biomass (sawdust, shavings, bark, chips). Therefore, its concept represents an opportunity for the forest industry and prompts the use of renewable, abundant, and inexpensive resources. However, to obtain products that are capable of competing with those manufactured from petroleum, a biorefinery demands an optimal use of the biomass, i.e., a proper fractionation into its main components (cellulose, hemicelluloses, and lignin), which could be used to obtain high-value-added products [1].

The selection of the type and severity of the fractionation treatments is assessed as a function of biomass nature and chemical composition, involving cost, carbohydrates recovery, and the final use of the obtained material [2]. In the case of softwoods, particularly pines, an efficient fractionation is especially difficult, as they are more recalcitrant than hardwoods and non-woods (bagasse, straws, rice husk, etc.). Therefore, the technically feasible, environmentally friendly, and economically viable valorization of pine sawdust represents a challenge. Numerous strategies have been assessed to fractionate pine sawdust, including hydrothermal treatments, steam explosion, alkaline treatments, and organosolv pulping with and without catalysts, etc. [3–7].

Alkaline treatments are widely used as delignification processes to obtain cellulosic pulp at an industrial scale. The most widespread alkaline process, kraft pulping, owes

its popularity mainly to its short pulping periods, high yields, flexibility regarding raw materials, and recovery of cooking chemicals [8]. However, the high scales required and the environmental issues caused by sulfur compounds have encouraged studies on sulfur-free pulping. In the biorefinery framework, a minimum environmental impact of the fractionation strategy is pursued. Then, the soda process assisted with anthraquinone (soda–AQ) represents an alternative of interest to conventional kraft pulping. Currently, this process is used on an industrial scale to obtain cellulosic pulp from non-woods. The benefits of anthraquinone (AQ) as a pulping additive lie in its redox action to both accelerate the delignification reactions and simultaneously preserve the carbohydrates (yield of pulp) under severe alkaline pulping conditions [9]. As a first step, AQ stabilizes the reducing end groups of carbohydrates against the peeling reactions, then turns into a reducing form, anthrahydroquinone (AHQ), which is soluble in the alkaline medium. Following this step, AHQ reduces the lignin, making it more reactive, and forms AQ again [10]. Soda–AQ pulping has been successfully tested on pine sawdust, achieving degrees of delignification as high as 92.9%, although lower than those obtained during kraft pulping under similar conditions [11]. Despite the effectiveness of AQ, its acceptability decreased during the last decade. It was pointed out as a carcinogenic chemical by different organisms from the USA and the European Union, limiting or banning its use as a pulping additive [12]. This regulatory context has set a new scenario for alkaline pulping with additives, and efforts are focused on finding new suitable sulfur-free processes.

Relevant research has been addressed in alkaline pulping assisted with organic solvents. Previous work on this subject has concluded that the addition of alcohol during alkaline pulping increases the extent of delignification and the process selectivity over conventional soda and kraft pulping [13]. Norman et al. performed a screening over a series of organic solvents to find those that render a positive effect on delignification, trying to clarify which solvent properties were required to achieve this improvement [14]. They concluded that most of the tested solvents prove an increase in the extent of delignification in soda, soda–AQ, and kraft pulping as well as suggested that solvents do not alter the chemical reactions of lignin. Therefore, their positive effect on delignification is mainly due to changes in the cooking liquor properties. Alkali–methanol cooking was studied in-depth by researchers from the University of Tokyo and the Japan Pulp and Paper Research Institute [15–18]. They aimed to elucidate the behavior of lignin and carbohydrates during alkali–methanol pulping. Daima et al. postulated that the solvent prevents lignin condensation through the active benzyl alcohol group methylation [17]. However, methanol shows several drawbacks regarding its toxicity, flammability, and low boiling point, which threaten the economic feasibility of alkali–methanol cooking [19]. In this context, ethanol stands as a promising additive for alkaline pulping. The ethanol-reinforced alkaline pulping was patented by Marton and Granzow in 1982 [20]. They found that adding ethanol to a soda cook significantly improves the selectivity towards lignin and stated that the chips pulped with this process were easier to defiberize than those obtained from soda or kraft pulping. The presence of ethanol in the pulping liquor promotes surface tension reduction, facilitating the penetration of the active chemicals into the material and the diffusion of the reaction products to the liquor [21]. Moreover, due to its high selectivity towards lignin, the soda–ethanol pulping performance has been evaluated on many raw materials (rice husk, spruce, sugarcane bagasse, *Arundo donax* L. reed) [22–24], but little is known regarding its efficacy with pine.

Similar to the traditional process, the soda–ethanol process also has the advantage of possessing a reagent recovery scheme. It involves the recovery of ethanol by a flash condenser in the depressurization of the reactor and from the condensates of black liquor evaporators. Both streams are combined and passed to a distillation column to obtain 96 wt% ethanol. Recovery of NaOH from concentrated black liquor presents the same stages of the soda process.

Soda–ethanol pulping of pine sawdust is proposed as the delignifying step in a fractionation strategy. Two experimental designs were carried out to study the influence of

ethanol–water ratio, alkaline load, and time at the maximum temperature on the extent of delignification, carbohydrates loss, yield, and chemical composition of the pulps. The results obtained for soda–ethanol pulping were statistically analyzed and compared with those obtained for soda–AQ and kraft pulping of pine sawdust.

2. Materials and Methods

Pinus elliottii and *Pinus taeda* sawdust mixture from a local sawmill was the raw material for the soda–ethanol pulping. The material was air-dried and sieved to uniform the particle size. The sawdust fraction passing through the 5×5 mm screen and retained in the 3×3 mm screen was used in all of the experiments. The material was stored in plastic bags to avoid moisture variations.

As industrial sawdust mix is contaminated with bark, sawdust samples were impregnated with water overnight to eliminate bark particles by flotation before each experiment.

Soda–ethanol experiments were performed in a 7 L pressurized reactor (M/K Systems, Inc., Williamstown, MA, USA), with indirect heating and liquor circulation, using about 500 g of dry sawdust in each experiment. After pulping, the pulps were filtrated to separate the spent liquors. Pulps were subjected to a five-cycle washing process with water, screened through a Somerville device, placed in sealed plastic bags, and stored under refrigeration. Yield determination and chemical analysis of the solid fraction were performed in all of the cases.

Liquor–wood ratio (L:W = 5.4:1), maximum temperature (170 °C), and time at maximum temperature (60 min) were held constant in all of the experiments. Two different experimental designs were used to assess the impact of the variation of the ethanol–water ratio (%*v/v*), alkaline (NaOH) load over dry wood mass (%odw), and time at maximum temperature (min).

The extent of delignification and the carbohydrates loss were calculated in accordance with Equations (1) and (2), respectively. All of the contents are expressed as %odw.

$$Extent \; of \; delignification \; (\%) = 100 \times \frac{Initial \; Lignin \; Content - Final \; Lignin \; Content}{Initial \; Lignin \; Content} \quad (1)$$

$$Carbohydrates \; Loss \; (\%) = 100 \times \frac{Initial \; Carbohydrate \; Content - Final \; Carbohydrate \; Content}{Initial \; Carbohydrate \; Content} \quad (2)$$

The selectivity of each treatment was calculated to evaluate its variation with the studied variables and to identify the conditions that favor high levels of delignification with low carbohydrate loss (Equation (3)).

$$Selectivity = \frac{Extent \; of \; delignification \; (\%)}{Total \; Carbohydrate \; Loss \; (\%)} \quad (3)$$

A factorial design was used to define the ethanol–water ratio (ethanol:water, %*v/v*) by assessing the effect of this variable combined with the alkaline load (*AL*, %odw) on pulping results and the chemical composition of pulps. Table 1 shows the tested conditions. For experiments A to F, the time at maximum temperature was 140 min. The central point (Experiments E and F) was run in duplicate to estimate the experimental error.

A 3^2 experimental design was performed over a wide range of alkaline loads (*AL*, %odw) and time at maximum temperature (t_{max}, min) to evaluate the delignification effectiveness of the soda–ethanol process for pine sawdust delignification. *AL* and t_{max} were tested at three levels, whereas the ethanol–water ratio was held constant (35:65 % *v/v*) for all of the experiments (conditions in Table 2). The central point was assayed five times to estimate the experimental error.

Table 1. Simple factorial design to evaluate the effect of ethanol–liquor ratio and alkaline load on the soda–ethanol pulping of pine sawdust.

Experiment	Ethanol:Water % *v/v* [1]	Alkaline Load %odw [2]
	(Code)	(Code)
A	35:65 (+1)	27.6 (+1)
B	35:65 (+1)	19.0 (−1)
C	10:90 (−1)	27.6 (+1)
D	10:90 (−1)	19.0 (−1)
E	22.5:77.5 (0)	23.3 (0)
F	22.5:77.5 (0)	23.3 (0)

[1] %*v/v*: Percentage in volume; [2] %odw: Over dry wood mass.

Table 2. The 3^2 experimental design.

Experiment	Time Min	Alkaline Load %odw [1]
	(Code)	(Code)
1	60 (−1)	19.0 (−1)
2	60 (−1)	27.6 (+1)
3	140 (+1)	19.0 (−1)
4	140 (+1)	27.6 (+1)
5	100 (0)	19.0 (−1)
6	60 (−1)	23.3 (0)
7	140 (+1)	23.3 (0)
8	100 (0)	27.6 (+1)
9 (×5)	100 (0)	23.3 (0)

[1] %odw: Over dry wood mass.

Statistical analysis of results was performed using Statgraphics Centurion XV software at 95% significance ($p < 0.05$).

The soda–ethanol pulping performance was compared with the two conventional pulping processes under similar operational conditions (soda–anthraquinone (soda–AQ) and kraft pulping). The conditions tested in each case are shown in Table 3.

Table 3. Conditions of kraft and soda–AQ pulping used for comparative purposes.

	Soda–Ethanol	Kraft	Soda–AQ
Alkaline Load (%odw) [1]	23.3	23.3	23.3
Sulfidity (%odw) [1]	-	18.6	-
AQ (%odw) [1]	-	-	0.1
T_{max} (°C)	170	170	170
Time at T_{max} (min)	100	100	100
L:W	5.4	5.4	5.4

[1] %odw: Over dry wood mass.

The chemical composition of the debarked sawdust and the solid fractions obtained in each experiment were determined.

The ash content and the water and ethanol extractives of the debarked sawdust mix were measured, in accordance with the Laboratory Analytical Procedure (LAP), Technical Reports of the National Renewable Energy Laboratory (NREL) "Determination of Ash in Biomass" (NREL/TP-510-42622), and "Determination of Extractives in Biomass" (NREL/TP-510-42619).

Acid-insoluble lignin (Klason lignin) and structural carbohydrates were determined following the procedure proposed by the technical report "Determination of Structural Carbohydrates and Lignin in Biomass" (NREL/TP-510-42618). Hydrolysate samples from the abovementioned technique were neutralized with $Ba(OH)_2$ following the methodology proposed by Kaar et al. [25]. HPLC with a SHODEX SP810 column was used to determine

the carbohydrate contents (glucans, xylans, mannans, galactans, and arabinans). The operational conditions used were water as eluent, 0.6 mL/min, 85 °C, and refractive index detector. The acetyl groups in sawdust and pulps were determined from the quantification of acetic acid in the hydrolyzate using an Aminex-HPX87H column (BIO-RAD), operated under the following conditions: 4 mM of H_2SO_4 as eluent, 0.6 mL/min, 35 °C, and Waters 996 HPLC Photodiode Array Detector at 210 nm.

The pulp kappa number was determined following the TAPPI T236 om-99 procedure, and the total yield (%) was calculated for every experiment.

3. Results

The chemical composition (%) of the debarked sawdust mix (mean and standard deviation) is glucans 40.9 ($\pm$0.5), xylans 7.45 ($\pm$0.10), galactans 2.58 ($\pm$0.07), arabinans 0.77 ($\pm$0.02), mannans 14.8 ($\pm$0.2), acetyl groups 1.22 ($\pm$0.02), insoluble lignin 29.2 ($\pm$0.1), water extractives 0.73 ($\pm$0.01), ethanol extractives 1.54 ($\pm$0.03), and ashes 0.04 ($\pm$0.00).

3.1. Simple Factorial Design: Effect of Ethanol–Liquor Ratio and Alkaline Load

A simple factorial design with two factors (Table 1) was used to understand the effect of the ethanol–water ratio (ethanol:water) and its interaction with the alkaline load (*AL*, %odw). Results are summarized in Table 4.

Table 4. Total yield, kappa number, and chemical composition of pulps from the simple factorial design.

Experiment	A	B	C	D	E	F
Yield (%)	39.1	46.1	40.6	45.8	41.5	41.3
Kappa Number	22.0	43.4	32.4	61.4	28.4	30.1
Delignification (%)	96.7	91.3	93.0	86.6	94.4	94.1
Selectivity	2.16	2.40	2.11	2.10	2.15	2.09
Klason Lignin (%odp) [1]	2.47 $\pm$ 0.11	5.53 $\pm$ 0.13	5.03 $\pm$ 0.11	8.52 $\pm$ 0.05	3.94	4.16
Glucans (%odp) [1]	79.6 $\pm$ 0.60	73.6 $\pm$ 0.29	80.1 $\pm$ 0.51	71.4 $\pm$ 0.39	76.7	75.6
Xylans (%odp) [1]	6.27 $\pm$ 0.53	8.79 $\pm$ 0.09	5.67 $\pm$ 0.21	7.66 $\pm$ 0.13	6.56	6.53
Galactans (%odp) [1]	0.40 $\pm$ 0.27	0.66 $\pm$ 0.29	0.00	0.72 $\pm$ 0.08	0.30	0.37
Mannans (%odp) [1]	9.16 $\pm$ 0.34	7.87 $\pm$ 0.12	7.42 $\pm$ 0.17	7.08 $\pm$ 0.08	8.00	7.60
Arabinans (%odp) [1]	0	0	0.00	0.00	0.00	0.00

[1] %odp: Over dry pulp mass.

The extent of delignification is positively affected by both factors (mainly by the alkaline load), but not by their interaction, as shown in Equation (4) (R^2 = 87.3%, regression model in codified independent variables).

$$Extent\ of\ Delignification\ (\%) = 92.7 + 2.10 * (Et:H20) + 2.95 * (AL) \qquad (4)$$

Increasing levels of ethanol in the cooking liquor ease the delignification process. This tendency has been previously reported by Shatalov et al. [24]. The authors, working with soda–ethanol pulping of *Arundo donax* L. reed, proved the beneficial effect of ethanol addition on lignin removal. In addition, they stated that the ethanol in the cooking liquor reduces its surface tension, improving the mass transfer of active chemicals (increasing the hydroxide ion concentration in the fiber) and degradation products. Moreover, the ethanol hinders the condensation reactions of lignin by the alkylation of the benzyl alcohol groups [26]. Other authors found that the addition of a low alcohol content (4%) to the alkaline liquor increased the delignification speed in the soda pulping of Pinus sylvestris wood, which allows for the reduction of alkaline charge to achieve the same degree of delignification for the same conditions of time and temperature [27].

The total pulp yield and the selectivity are not affected by the ethanol–water ratio, in contrast to the statements of the other authors. When working with ethanol–kraft pulping of aspen and spruce chips, Yoon et al. [28] found a significant gain in pulp yield with the increasing ethanol content in cooking liquor.

Regarding the chemical composition, acid-insoluble lignin depends on both variables (R^2 = 88.2%). The contents of glucans, xylans, and galactans in pulps are affected by the *AL* (R^2 = 94.8, 78.8, and 70.3%, respectively), but not by the ethanol–liquor ratio.

3.2. 3^2 Design: Effect of the Alkaline Load and Time at Maximum Temperature

The effect of the alkaline load was studied in-depth, together with the effect of time, using a 3^2 design. The obtained results of each experiment are summarized in Table 5. Experiment 9 (central point) is the mean value of five replicates.

Table 5. Total yield, kappa number, and chemical composition of the solid materials from the 3^2 design.

Experiment	1	2	3	4	5	6	7	8	9
Yield (%)	49.9	45.6	46.1	39.1	46.5	46.2	40.5	41.0	43.6
Delignification (%)	82.6	92.8	91.3	96.7	88.8	89.3	94.9	94.7	93.8
Kappa Number	70.8	34.6	43.4	22.0	50.9	47.3	25.5	25.3	29.9
Selectivity	2.33	2.36	2.40	2.16	2.38	2.44	2.24	2.29	2.28
Klason Lignin (%odp) [1]	10.2 ± 0.17	4.61 ± 0.02	5.53 ± 0.13	2.47 ± 0.11	7.04 ± 0.39	6.75 ± 0.35	3.67 ± 0.04	3.77 ± 0.02	4.12 ± 0.06
Glucans (%odp) [1]	68.6 ± 0.38	74.3 ± 0.60	73.6 ± 0.29	79.6 ± 0.60	74.1 ± 0.14	75.3 ± 0.84	80.7 ± 0.55	81.1 ± 1.60	74.6 ± 0.44
Xylans (%odp) [1]	9.71 ± 0.44	6.76 ± 0.35	8.79 ± 0.09	6.27 ± 0.53	8.64 ± 0.11	7.64 ± 0.18	6.97 ± 0.41	6.01 ± 0.56	8.31 ± 0.45
Galactans (%odp) [1]	1.23 ± 0.17	0.51 ± 0.28	0.66 ± 0.29	0.40 ± 0.27	0.73 ± 0.24	1.07 ± 0.05	0.28 ± 0.11	0.47 ± 0.28	0.56 ± 0.40
Mannans (%odp) [1]	7.38 ± 0.49	8.48 ± 0.24	7.87 ± 0.12	9.16 ± 0.34	7.58 ± 0.08	80.76 ± 0.17	8.13 ± 0.14	9.11 ± 0.38	7.78 ± 0.19
Arabinans (%odp) [1]	0.50 ± 0.01	0	0	0	0	0	0	0	0

[1] %odp: Over dry pulp mass.

All of the experiments render a well-delignified material. The total yield varied between 39.1% (Experiment 4) to 49.9% (Experiment 1), and the statistical analysis reveals a strong dependence on *AL*, t_{max}, and their interaction.

The information provided by statistical models is crucial for understanding the behavior of the individual components of the raw material, optimizing the operational variables, and shaping the characteristics of the final product.

The experimental values of the total yield were adjusted to a regression model in codified independent variables (Equation (5), R^2 = 96.7%). The curves estimated by the model are plotted in Figure 1.

$$Total\ Yield\ (\%) = 43.5 - 2.67 * (t_{max}) - 2.79 * (AL) - 0.67 * (t_{max}) * (AL) - 1.18 * (AL)^2 \tag{5}$$

The influence of the *AL* on total yield is more noticeable at a higher time at maximum temperature. The difference in total yields for experiments carried out at 19.0 and 23.3% *AL* is slightly higher than the difference exhibited by experiments conducted at 23.3 and 27.6% *AL*.

The delignification for each experiment was calculated in accordance with Equation (1). The maximum extent of delignification (96.7%) and the lowest yield (39.07%) were achieved using the most severe conditions (Experiment 4). All of the studied factors significantly affected the extent of delignification. The experimental results were adjusted to a second-order model using codified independent variables (Equation (6), R^2 = 98.6%). The curves estimated by the model are plotted in Figure 2.

$$Extent\ of\ Delignification\ (\%) = 93.7 - 3.03 * (t_{max}) - 3.59 * (AL) - 1.34 * (t_{max})^2 - 1.19 * (t_{max}) * (AL) - 1.70 * (AL)^2 \tag{6}$$

All of the studied factors proved to have a significant effect on the delignification extent. Time at maximum temperature has more impact on treatments with an alkaline load of 19.0%odw: Small changes in time rendered relevant changes in delignification. At higher *AL*, the impact of time weakens.
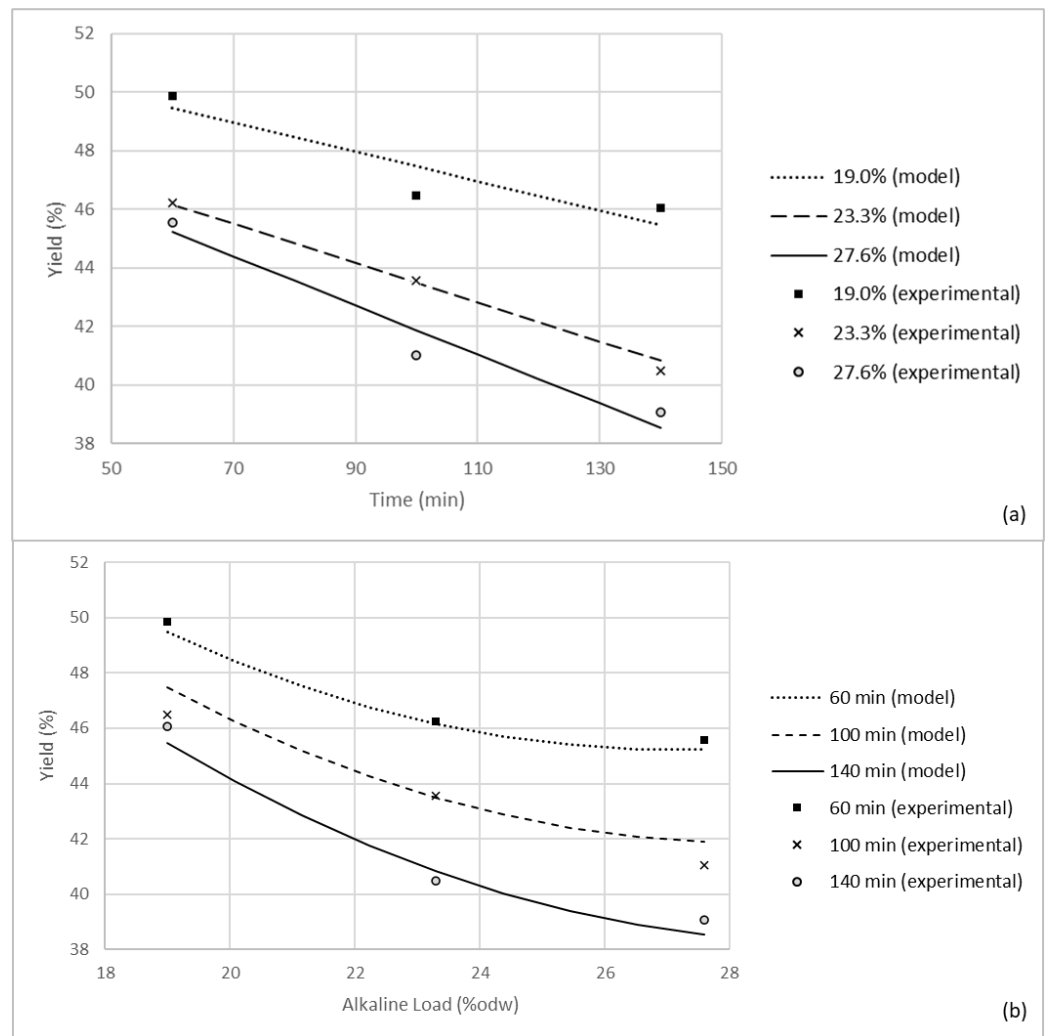
Figure 1. Total yield of the soda−ethanol delignification of pine sawdust (**a**) as a function of time for three levels of alkaline load (%odw); (**b**) as a function of alkaline load for three levels of time (min).
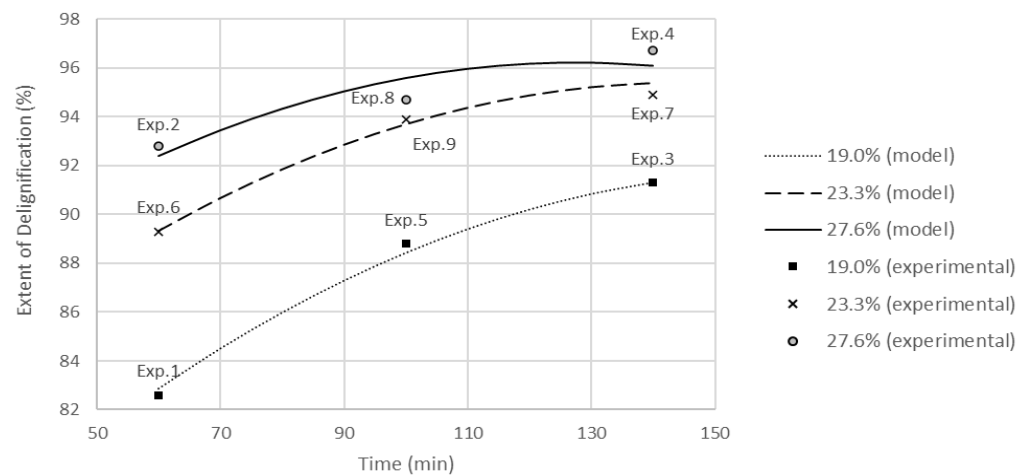

Figure 2. Extent of delignification as a function of time (min) and alkaline load (%odw) for the soda−ethanol delignification of pine sawdust.

The model predicts an increase in barely of 1.26% on the extent of delignification for 140 min-treatments at 23.3 and 27.6 %odw *AL*, probing that the effect of *AL* decreases when cooking for long periods.

In accordance with the statistical model, the treatment with an alkaline load of 27.6 %odw reaches its maximum delignification at about 127 min.

The desirability function identifies the combination of factors that simultaneously optimize multiple answers. This function, expressed on a scale from 0 to 1, was used to maximize both the total yield and the extent of delignification (Figure 3). The maximum desirability is 0.68 and is achieved at the conditions of Experiment 2, i.e., 60 min at maximum temperature and an alkaline load of 27.6 %odw.
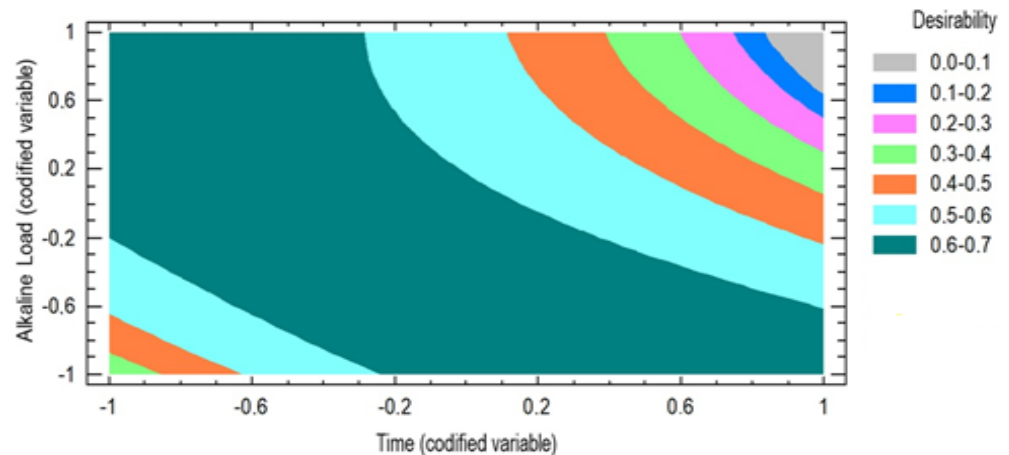
Figure 3. Desirability function to maximize yield and delignification.

Figure 4 shows the evolution of the total yield and the extent of delignification with the alkaline load and cooking time. The plotted curves are a powerful tool for adjusting the operational variables to obtain a target outcome.
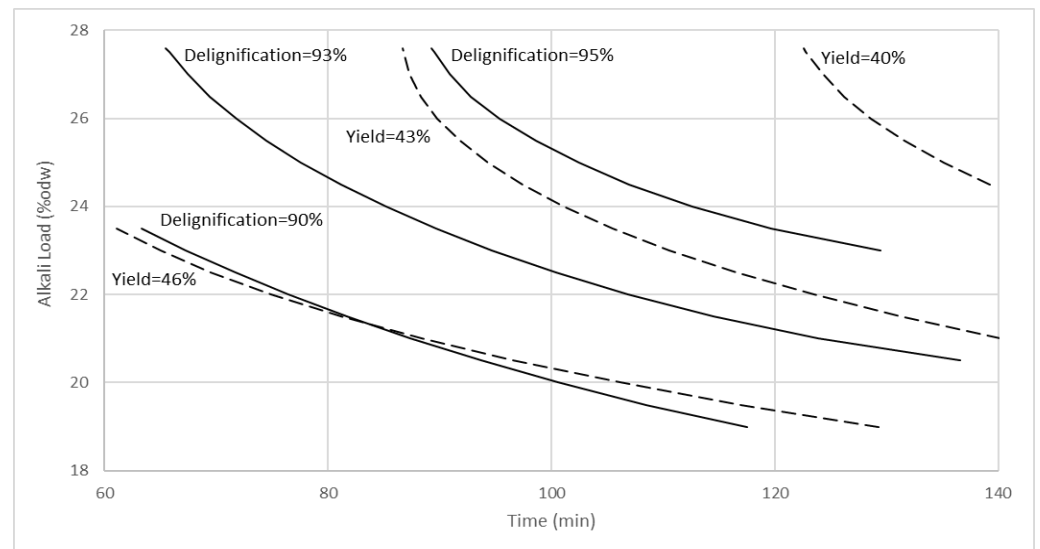

Figure 4. Variation of yield and delignification with alkaline load (%odw) and time (min) at maximum temperature (yield: Plain line; delignification: Dashed line).

The selectivity, defined herein as the ratio between the extent of delignification and the total carbohydrate loss (Equation (2)), is significantly affected by AL, t_{max}, and their interaction. The experimental selectivities are plotted in Figure 5.
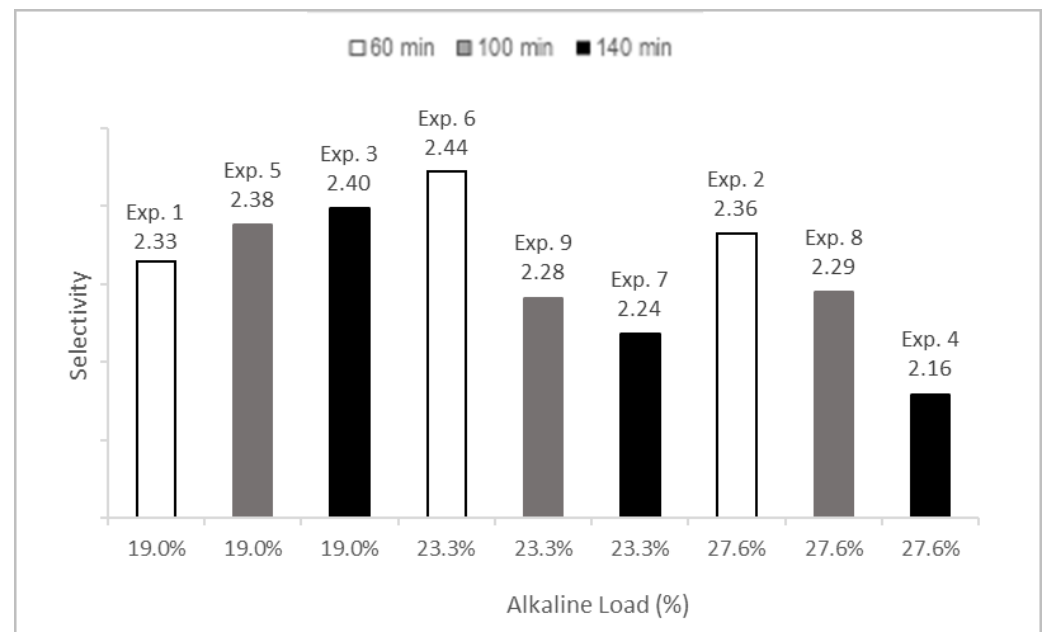
Figure 5. Selectivity for the soda−ethanol delignification of pine sawdust.

Selectivity is strongly affected by the AL-t_{max} interaction. When working at low AL (19.0%), increasing the time at maximum temperature produces a slight increase in selectivity. Moreover, this tendency applies to the degree of delignification, which implies that carbohydrates are better preserved at low AL, even for long periods at maximum temperature (140 min-treatment). Therefore, when using a low alkaline load, it is possible to obtain high levels of delignification by increasing the cooking time without selectivity loss. On the contrary, when using higher alkaline loads, t_{max} increase causes relevant selectivity loss. In severe conditions, delignification increases of approximately 6% and 4% for AL = 23.3% and AL = 27.6%, respectively, correspond to a selectivity loss of about 8%. This information is relevant when evaluating the economics and the environmental impact of the process regarding energy requirements and chemical consumption.

The pulps' chemical composition was determined, and statistical analysis was performed for each component. During the soda−ethanol treatment of pine sawdust, the glucans, xylans, and galactans (expressed as %odw) decrease, when the AL and t_{max} increase. The mannans content, which ranged between 3.29 and 4.05 %odw, did not show a statistical dependency on the studied factors.

The experimental values of acid-insoluble lignin and total carbohydrates content of pulps, expressed as %odw, were adjusted to regression models (R^2 = 98.8% and 95.5%, respectively), as shown in Equations (7) and (8), respectively.

$$Acid\ Insoluble\ Lignin\ (\%odw) = 1.83 - 0.88 * (t_{max}) - 1.05 * (AL) + 0.39 * (t_{max})^2 + 0.35 * (t_{max}) * (AL) + 0.50 * (AL)^2 \quad (7)$$

$$Total\ Carbohydrate\ Content\ (\%odw) = 40.1 - 1.58 * (t_{max}) - 1.62 * (AL) + 0.43 * (t_{max})^2 - 0.51 * (t_{max}) * (AL) + 0.55 * (AL)^2 \quad (8)$$

By expressing the chemical compositions as % over dry wood mass, it is possible to understand how the process conditions affect each component, regardless of the behavior of the others. Both parameters depend on the AL, t_{max}, the interaction AL-t_{max}, and the quadratic effect of both variables.

Figure 6 shows the total carbohydrate content (TCC) and the acid-insoluble lignin (AIL) behavior, in accordance with the regression models (Equations (7) and (8)). When working with low alkaline loads (19.0 %odw), AIL decreases sharply with time, while TCC exhibits a smooth variation (Region I: This explains selectivity values at 19.9 %odw AL. However, in agreement with selectivity values for higher alkaline loads, AIL curves

for 23.3 %odw and 26.7 %odw *AL* flatten when time increases above 120 and 140 min, respectively, while TCC continues to decrease (Region II).
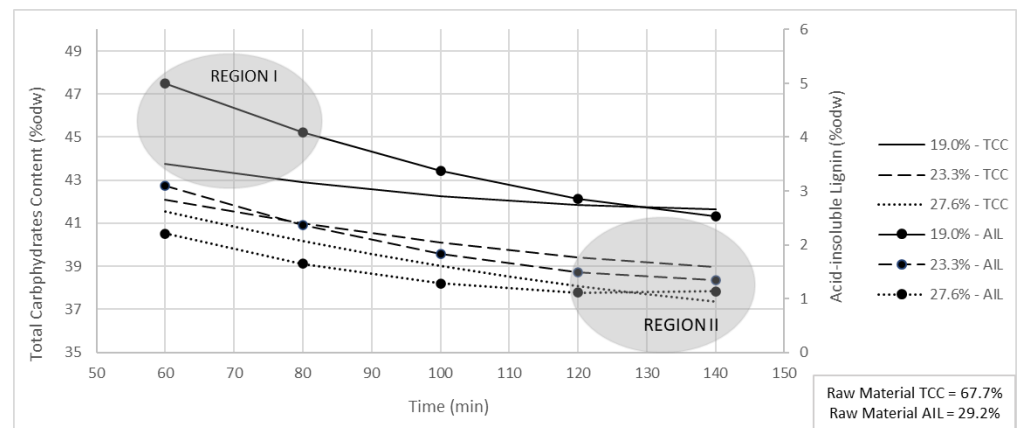

Figure 6. Total carbohydrate content (TCC) and acid-insoluble lignin (AIL) vs. time. Raw materials TCC and AIL are expressed as % over dry debarked sawdust mass.

The kappa number is widely used in the pulp industry as a quick and reliable method to determine the residual lignin in pulp. This parameter was measured and adjusted to a regression model (R^2 = 99.7%), as shown in Equation (9). Figure 7 is a helpful tool if cooking at a target kappa number, as it allows for the fixation of the operational variables that fulfill that requirement.

$$Kappa\ number = 30.2 - 10.3 * (t_{max}) - 13.9 * (AL) - 3.71 * (t_{max}) * (AL) - 7.26 * (AL)^2 \tag{9}$$
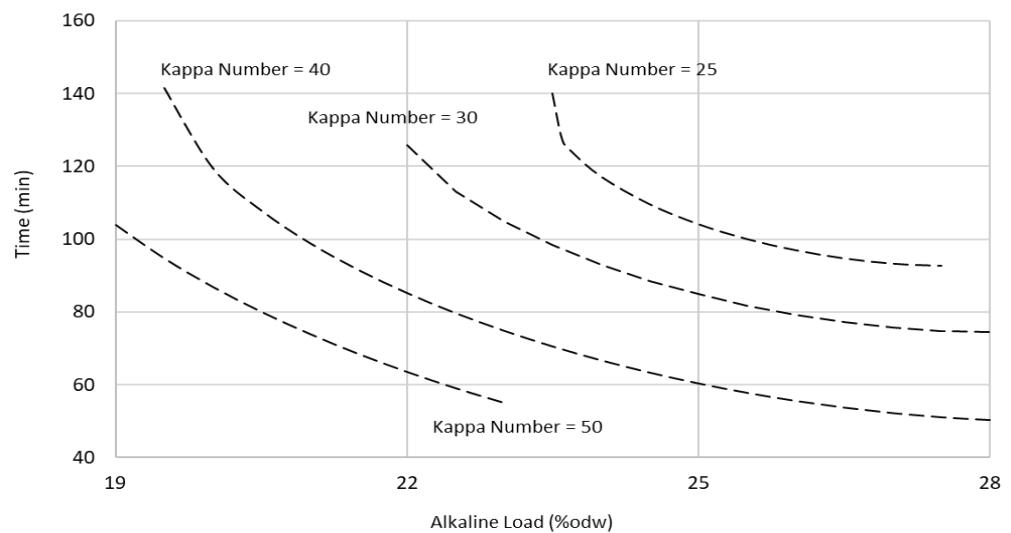

Figure 7. Regression model for the kappa number.

The ethanol–water process arose as an alternative to the kraft process, but ethanol pulping requires extreme conditions. For example, the Alcell process treats wood with 50% (weight–weight) ethanol–water at temperatures of 190–200 °C, corresponding to an operating pressure of 400–500 psig [29]. On the contrary, this work presents an ethanol–soda system with a lower amount of ethanol (35% vol/vol) and the usual kraft pulping temperature (170 °C), resulting in a pressure of about 180 psig. It has the advantages of both systems, soda and ethanol. These treatment conditions are referred to as "mild conditions".

Soda–ethanol pulping of pine sawdust results were compared to the kraft and soda–AQ pulping performed in the conditions of the central point of the 3^2 design (Table 2) and

using the same raw materials (Table 6). In addition, the central point was performed on pine chips.

Table 6. Comparison between the soda–ethanol process (point 9) and conventional pulping processes of pine sawdust and pine chips (Pinus taeda).

Experiment	Soda–Ethanol (Sawdust)	Soda–Ethanol (Chips)	Kraft	Soda–AQ
Yield (%)	43.6	45.0	43.4	46.4
Delignification (%)	93.9	92.9	94.6	92.6
Kappa Number	29.9	35.1	29.0	34.2
Selectivity	2.28	3.06	2.28	2.48
Klason Lignin (%odw) [1]	1.79 ± 0.03	2.21 ± 0.04	1.58 ± 0.03	2.15 ± 0.03
Glucan (%odw) [1]	32.5 ± 0.19	36.48 ± 0.05	33.1 ± 0.22	34.6 ± 0.06
Xylan (%odw) [1]	3.62 ± 0.20	3.26 ± 0.03	3.40 ± 0.03	3.41 ± 0.05
Galactan (%odw) [1]	0.24 ± 0.17	0.25 ± 0.09	0.00	0.00
Arabinan (%odw) [1]	0.00	0.00	0.00	0.00
Mannan (%odw) [1]	3.39 ± 0.08	2.98 ± 0.08	3.10 ± 0.03	4.28 ± 0.03
Intrinsic viscosity in CED [30]	412 ± 1	470 ± 3	568 ± 4	502 ± 2
DP [2] [30]	783 ± 2	893 ± 6	1079 ± 8	954 ± 4
CI (%) [3] [30]	75.8	79.0	79.8	79.9

[1] %odw: Over dry wood mass; [2] polymerization degree; [3] crystallinity index.

At the conditions of the central point (100 min-treatment and 23.3 %odw of alkaline load), similar selectivities were achieved by kraft pulping and soda–ethanol delignification of pine sawdust, suggesting that soda–ethanol at mild conditions and the kraft process are equally efficient. However, due to its sulfur-free nature, the soda–ethanol process is a more suitable candidate for the delignification stage in a biorefinery scheme for pine sawdust, where a minimum environmental impact is a pursuit. In addition, the soda–ethanol process preserves more hemicelluloses than kraft pulping, which may be desirable, for example, to produce microfibrillated cellulose since they facilitate mechanical action, reducing energy consumption [30].

Compared with the soda–AQ treatment performed under the same conditions, the soda–ethanol process showed lower selectivity. However, it exhibited a lower delignification than soda–ethanol, which could probably be one reason for the higher carbohydrate preservation.

4. Discussion

Other authors have explored the performance of soda–ethanol pulping on various hardwoods, reeds, and grasses (Table 7). Although the chemical structure of lignin varies from one lignocellulosic material to another, the soda–ethanol treatment proves to be a suitable pulping method in a fractionation strategy for all of them, as it renders well-delignified pulps.

Soda–ethanol pulping performance of *Arundo donax* L. reed [26] showed similarities to pine sawdust in this work, which is relevant given the increasing character of softwoods. The authors found that the alkaline load increase led to residual lignin and yield drop, and the presence of ethanol in the liquor did not change this tendency. On the contrary, Shatalov et al. observed that selectivity and yield improved with ethanol addition [24].

Working with aspen chips, von Schenck et al. [27] proved that ethanol addition to the alkaline liquor delays the unselective residual phase without significant yield gain when increasing the ethanol proportion. For *Pinus sylvestris* chips, ethanol and AQ addition to the alkaline liquor both accelerate the delignification, but the AQ effect was higher than ethanol. The results proved otherwise: Although the soda–AQ selectivity was superior, soda–ethanol delignification was higher in the same mild conditions tested.

Table 7. Soda–ethanol treatment performance on other lignocellulosic materials.

Raw Material	Pretreatment	Soda–Ethanol Pulping Conditions			Delignification	Yield (%)	Reference
		Time	Temp.	Reagents			
Rise Husk	Diluted acid (0.3% *w/v* H$_2$SO$_4$; 152 °C; 33 min)	60 min	160 °C	13.0% NaOH— 50:50 ethanol:liquor	90.1% (acid-insoluble lignin 1.88 %odp)	57.63%	[31]
Sugar cane bagasse	–	90 min	195 °C	15.0% NaOH— 25.0% ethanol	Kappa Number = 12	45.30%	[32]
Sugar cane straw	–	90 min	175 °C	10.0% NaOH— 45.0% ethanol	Kappa Number = 12	43.90%	[32]
Cotton stalk	–	60 min	160 °C	18.0% NaOH— 50.0% ethanol	Kappa Number $\approx$ 49.3	41.49%	[23]
Arundo donax L. reed	–	180 min	140 °C	25.0% NaOH— 40:60 ethanol:liquor	Acid-insoluble and soluble lignin $\approx$ 4%	$\approx$52%	[26]
*Pinus pinaster*chips	–	90 min	170 °C	30.0%NaOH— 35.0% ethanol	Acid-insoluble lignin 2.8 %odw	44.35%	[33]

Moreira et al. results on *Pinus pinaster* chips are comparable with those obtained herein for *Pinus taeda* chips (Table 6). Similar yields and acid-insoluble lignin were achieved at 35:65 ethanol–water ratio and 170 °C, although higher *AL* was necessary for *Pinus pinaster* chips [33]. Del Rio et al. tested a single soda–ethanol pretreatment at 170 °C, 60 min, 20.0% NaOH, and 65:35 ethanol–water ratio on *Pinus contorta* chips. Comparing their results with Experiment 1 (60 min; 19.0 %odw *AL*), pulps with similar yields and AIL contents were obtained [34].

Soda–ethanol proved to be a suitable process for pulping pine sawdust. The cellulosic fraction can be used to produce Sdifferent products, such as bioethanol or nanocellulose [30]. The lignin is burned in the chemical recovery process, but could also be recovered. This study is beyond the scope of this work.

5. Conclusions

An exhaustive study using two experimental designs was conducted to establish the viability of soda–ethanol delignification of pine sawdust. The 3^2 experimental design revealed that it is possible to obtain a well-delignified material by subjecting pine sawdust to the soda–ethanol process. The conditions tested were not very different from those frequently used in conventional pulping at an industrial scale, suggesting the technical feasibility of this process.

Increasing levels of ethanol in the cooking liquor ease the delignification process of pine sawdust, but do not affect the total yield within the studied range.

At fixed ethanol–liquor ratio, the studied factors significantly influence total yield and delignification extent. Selectivity is strongly affected by the interaction of alkaline load and time at maximum temperature: Carbohydrates are better preserved at a low alkaline load (19.0%), even for long periods at maximum temperature, whereas the extent of delignification keeps increasing with time within the studied range. On the contrary, when applying higher alkaline loads, the lignin removal at the maximum temperature flattens above 100 min for an alkaline load of 23.3 and 27.6%. In addition, the total carbohydrate loss ratio exceeds the delignification extent. This information gains relevance in the economic and the environmental impact evaluation of the fractionation strategy that includes soda–ethanol pulping. Moreover, it allows for the tailoring of chemical consumption and energy requirements depending on the quality of the searched product.

Selectivity of soda–ethanol treatment of pine sawdust at mild conditions equals the selectivity of soda–AQ, exceeding the kraft process.

Soda–ethanol pulping was shown to be a suitable delignification stage for a biorefinery scheme of *Pinus elliottii* and *Pinus taeda* sawdust. It has many advantages over conventional processes regarding its environmental impact, harmless chemicals, and selectivity.

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