HEMICELLULOSES EXTRACTION FROM PINE SAWDUST: A KINETIC STUDY OF SPENT LIQUOR RE-USE

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ABSTRACT

Pine sawdust is an important lignocellulosic waste from the primary industrialization of wood in Argentina and Uruguay, so its valorization using the biorefinery platform could add new value chains into its forest industry. Hemicelluloses from lignocellulosic waste is abundant polymer with enormous potential for industrial applications. The chemical structure of the hemicelluloses allows their use as precursors for a wide range of chemicals such as alcohols, organic acids, and furanic compounds. In a biorefinery context, pine sawdust can be separated in a valuable cellulose solid fraction and the spent liquor. However, current alternatives for the valorization of hemicelluloses are commercially limited due to their high cost production. The spent liquor reuse for biomass deconstruction could be a promising strategy to reduce water usage in the system and capital and operating costs. However, it is necessary to perform experiments in order to evaluate how a concentrated extraction media can affect the hydrolysis process. The aim of this study was to analyze the re-use of the spent liquor in dilute acid pre-treatment for the hemicellulosic extraction and to determine a kinetic model of hexoses and pentoses solubilisation. Alkali pretreated pine sawdust was treated by dilute acid treatments to extract hemicelluloses (7.5 g/L H_2SO_4 at 150°C for 30 min and liquid to solid ratio 10:1). The spent liquor was re-used four times, in order to determine the variation in the sugar concentrations and their degradation compounds. The spent liquor composition from the diluted acid treatment was determined by HPLC. A simplified first order kinetic model for sugar release and decomposition was proposed. Using the experimental data of a diluted acid hydrolysis with fresh water, kinetic constants were obtained by parameter adjustment using maximum likelihood estimation method. The model was used to predict the sugar and degradation products of re-cycled experiments. Comparison between modelled and experimental data allows to say that the model suitably describes sugar solubilisation and decomposition. In order to consider the potential benefits *of the re-use strategy,* overall *costs has to be analyzed in a biorefinery context including the resulting cellulose quality. However, the results obtained in this work allow to say that more than two* recycles should *not be suitable for pentoses or its derived valuable chemicals, as pentoses are strongly degraded. It could be useful for glucose- derived chemicals, and furfural or its derived chemicals.*

Keywords: *Pine sawdust; Acid hydrolysis; Hemicelluloses, Spent liquor; Carboxylic acid.*

1. INTRODUCTION

Pine sawdust is an important lignocellulosic waste from the primary industrialization of wood in Argentina and Uruguay, so its valorization using the biorefinery platform could add new value chains into forest industry and can serve as a model for other countries. The global forest industry is focused on the development of technologies for waste reuse or valorization. Typical large-scale biorefinery scenario is based on the production of commodities, as the extraction of sugars from biomass to produce cellulosic ethanol, steam, and electricity. However, the production of diverse wood byproducts is crucial to have competitive producing costs [1, 2].

Pine hemicelluloses are mainly formed by galactoglucomannans, arabinoglucuronoxylan, and arabinogalactan. Their chemical structure allows their use as precursors for a wide range of chemicals such as alcohols, organic acids, and furanic compounds. However, current alternatives for the valorization of hemicelluloses are commercially limited due to their high cost production.

Bio-based chemicals from hemicelluloses would be an alternative to the products derived from oil. Levulinic acid is a platform-molecule which can be converted into derivable high-value-added chemicals. The commercial-scale production of levulinic acid from lignocellulosic materials requires of a cheap feedstock as forestry wastes (branches, foliage, and roots) or industrialized wood wastes (bark, sawdust, wood chips, and other residues) to compete with the petrochemical

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route [3]–[5]. Formic acid, acetic acid, and furfural are byproducts of the levulinic acid production. The global market of levulinic acid, formic acid, and furfural are expected to grow at a Compound Annual Growth Rate (CAGR) of 5.7 [6], 4.9 [7] and 11.6 % [8], respectively.

Pine sawdust represents an attractive raw material to produce high-value-added compounds, but its fractionation is complex due to its chemical composition, e.g. high content of resin acids, hemicelluloses, and guaiacyl type lignin which is not highly reactive [9].

Biorefinery is still in a development stage, especially due to production costs are still high compared with the production of similar products from oil [2]. The challenge faced is how to produce commodities and valuable chemicals using cost effective processes. Many efforts in this sense have been done, one special been the mass and energy integration [10], which has the aim of reduce water and energy consumption and by this means reduce costs.

In previous work [11], a single unit liquor reuse strategy was proposed to reduce the total production costs of added value products from degradation of solubilized sugars in the pretreatment processes of lignocellulosic materials. The basic idea is presented in Figure 1.
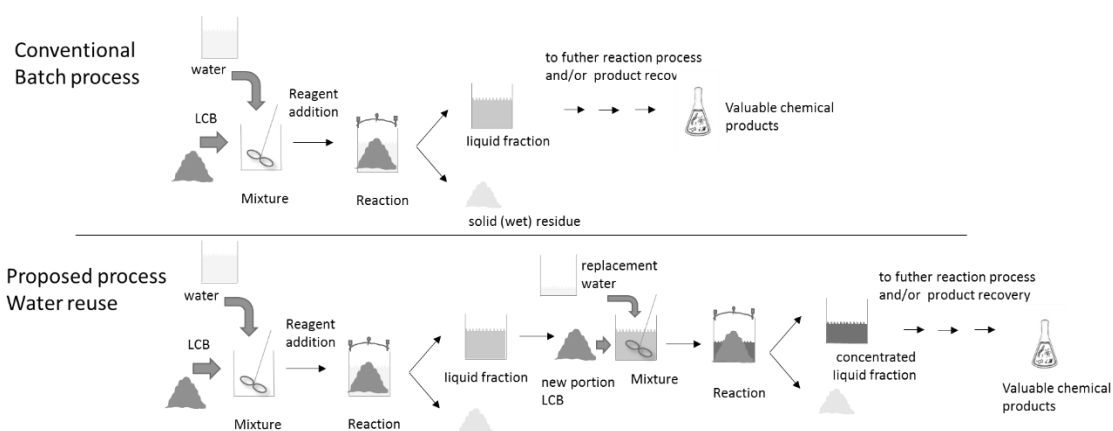

Figure 1: Scheme of proposed re-use in a single unit, applied in this case for pretreatment of biomass.

This strategy could reduce overall energy consumption, because we would obtain a liquor with more concentrated sugars which would imply a reduction in energy consumption for evaporation. In addition, the available heat in the liquor obtained in the pretreatment process (acid hydrolysis) for the following recycles would be taken advantage of. Re-use can be applied to pretreatment, as long as the desired product is not degraded at a rate that negatively affect production costs.

This recycle in a single unit represents a challenge in order to be included in an integration problem, because of its dynamic nature. Even when difficult to be theoretically described, it has the advantage of being physically simple, compared with recycle streams in a continuous scheme: liquor has not to be pumped nor distilled or flash separated.

As the number of re-uses increases, the liquor will become more and more concentrated in hydrolysed sugars, in their degradation products and also in other compounds that are removed from the saw dust (e.g. soluble organic compounds, salts.).

In this work, the following questions regarding this procedure are addressed: 1.- if the re-use of liquor affects the yield of sugar removal from sawdust 2.- If undesirable reactions (polimerization, precipitation, humin formation) will occurs. 3.- If the re-use of liquor affects the rate of hydrolysis and decomposition reactions

2. METHODS

2.1 Raw material
Alkali pretreated pine sawdust obtained in previous study (5% NaOH oven dry basis (od) at 90°C for 1 h)[12] was used as raw material. This treatment removed 90.7% of extractives with a yield of 92%. The chemical composition of the alkali pretreated sawdust was determined in previous work of our group [12,13]: 41.2% glucans, 6.4% xylans, 1.7% galactans, 1.0% arabinans, 9.0% mannans, 0.4% total extractives, and 26.3 % lignin.

2.2 Dilute acid treatment with spent liquor reuse

Dilute acid treatments of alkali pretreated pine sawdust were performed based on the optimal operational conditions for the maximum hemicelluloses extraction determined by Stoffel et al., 2014 [12]: 7.5 g/L H_2SO_4 at 150°C and liquid to solid ratio 10:1 [12].

Experiments for kinetic model parameter estimation.

Experiments were conducted during 90 min, in order to obtain proper data for degradation products. Samples were taken periodically for chemical analysis.

Experiments for liquor re-use evaluation

Each pre-treatment was carried out for 30 min. After pretreatment, spent liquor was separated from the wet solid. Wet solid was washed, dried and weighted. Total liquid volume of experiments was 120 ml. After pre-treatment, a measured amount of spent liquor (75-80 ml) was recovered and reused. In order to compensate the amount of liquor that was removed with the solid, a 40-45 ml of fresh diluted acid and acid was added until to reach the conditions of the pretreatment. The spent liquor was reused five times, in order to determine the variation in the sugar concentrations and their degradation compounds.

Pre-treatment yield was calculated as

$$Y = \frac{M_f}{M_o}$$

Where M_f is the amount of dry solid obtained after pre-treatment and M_o is the initial dry mass of sawdust.

2.3 Chemical analysis of spent liquor

After the diluted acid treatment, the solid fraction (mainly cellulose) was filtered to separate the liquid fraction (spent liquor), rich in hexoses (mannose, glucose and galactose) and pentoses (xylose and arabinose) derived from hemicelluloses.

The spent liquors composition from the diluted acid treatment was determined according to the Laboratory Analytical Procedure (LAP), Technical Reports of the National Renewable Energy Laboratory (NREL) "Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples" NREL/TP-510-42623. Samples were neutralized with $Ba(OH)_2$. Mannose and galactose were determined by HPLC with a SHODEX SP810 column using water as eluent, 0.6 mL/min, 85°C, and refractive index detector. Xylose, arabinose, acetic acid and degradation products (furfural and HMF) were quantified by HPLC with an Aminex-HPX87H column under the following operational conditions: 4 mM of H_2SO_4 as eluent, 0.6 mL/min, 35°C, with a diode array detector.

2.4 Kinetic model

Kinetic models have been applied to describe acid hydrolysis process for different treatment conditions. The kinetics of the hydrolysis reaction for extraction of hemicelluloses from pine sawdust using diluted acid has been little studied [14, 15]. The model proposed in this study is an adaptation of the irreversible first-order model developed by Saeman [16, 17] designed for the acid hydrolysis of cellulose from Douglas for wood, which predict the formation of glucose from cellulose and its degradation. This simple model does not take into account crystallinity of cellulose nor the diffusion of acid. The changes in the composition of spent liquor during the acid treatment were taken into account to design and optimize the conversion processes from hemicelluloses to hemicellulosic sugars. The general model of Saeman can be applied to other homopolymers where the monomer is sequentially released and degraded [16]. This kinetic model was used to predict the solubilization of hexoses (and pentoses) present in sawdust in to liquor which is degraded to hidroxymetilfurfural (HMF) (and furfural for pentoses), and other degradation products (Eq. 1).

$$C_C \xrightarrow{k_1} C_P \xrightarrow{k_2} C_D \tag{1}$$

Where:
C_c is the hemicelluloses content in pine sawdust
C_P is the hexoses (or pentoses) content in the spent liquor
C_D is HMF (or Furfural) content in the spent liquor
k_1 is the first order kinetic constant for polymer (cellulose or hemicellulose) hydrolysis, and k_2 is the first order kinetic constant for sugar degradation reaction (HMF for hexoses or Furfural for pentoses).

This set of a batch reaction in series leads to a set of two ordinary differential equations (ODEs), for C_P and C_D evolution along time. The solution of this ODE system has an analytical solution described in Eq. 2 to Eq. 4 considering an initial condition of C_0 (g/L), the initial concentration of sugars (hexoses or pentoses) content in the spent liquor; and C_{Po} (g/L) is the initial sugars content in the sawdust, expressed as grams of equivalent monomer per liter of spent liquor .

$$C_P(t) = C_o e^{-k_2 t} + C_{Po} \alpha \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{2}$$

$$C_D(t) = j/k_1 (1 - e^{-k_1 t}) - j/k_2 (1 - e^{-k_2 t}) \tag{3}$$

$$j = \frac{k_1 k_2 \, f \, \alpha \, C_{Po}}{k_2 - k_1} \tag{4}$$

Where: (i) j is a combined factor derived from the resolution of the differential equation, (ii) α is the fraction of glucans (xylans) that can be transformed in glucose (pentoses), according to Aguilar *et al,* [18], and (iii) f is a conversion factor glucose to HMF molecular weight ratio for hexoses (1.42) and xylose to furfural molecular weight ratio (1.136),

Kinetic constants k_1, k_2 *and* α were determined by maximum likelihood estimation using a nonlinear optimization method of generalized reduced gradient.

3. RESULTS AND DISCUSSION

Pre-treatment yield and concentrations of total hemi-cellulosic sugars and degradation products in the spent liquor are shown in Table 1. The results of the column 0 is the first test performed (with fresh diluted acid)

Table 1. Yield, total hemi-cellulosic sugars and degradation products in the spent liquor.

Reuse	Concentration of residual liquor (g/L)				
	0	1	2	3	4
Total yield (g/g)	0,80	0,81	0,83	0,84	0,85
Total sugars	14,0	22,8	29,6	32,3	33,4
HMF	0,04	0,25	0,38	0,51	0,57
Furfural	0,52	2,56	3,81	4,76	5,20

Yield of diluted acid treatments slightly increased with the number of reuses. The yield of first and second reuse were similar, however, a slight increase was observed after the second reuse.

Hexoses and pentoses concentration in the spent liquor for re-uses 0 to 4 is shown in Figure 2. The reuse of the spent liquor increased significantly the total sugar concentration with the first and second reuse. After the third reuse, no significant changes were observed in the concentration of sugars. The increase in the concentration of sugars was mainly due to the increase in the concentration of hexoses. Even when the suitable number of re-uses for a given final product will be decided on a cost basis, from Figure 2 it can be seen that no more of 3 recycles will be profitable.

In each cycle, the hexoses extraction was around of 52% and pentoses 63% of the available hemicelluloses in alkali pretreated sawdust. Sugars extraction between cycles was the same, however, due to the dilutions effect between the recycles, the increase in concentration was lower.

Pentoses and hexoses extracted (g/L)

Glucose   Galactose   Mannose   Xylose   Arabinose
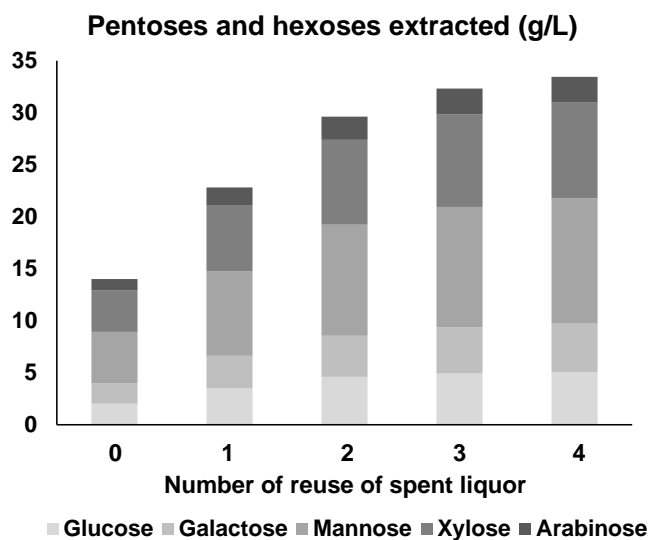
Figure 2: The concentrations of hexoses and pentoses in the spent liquor in the different reuses.

These experimental data of sugar and degradation products were used to determine the kinetic constants k_1 and k_2. The results are presented in Table 2.-

Table 2. The kinetic constants k_1 and k_2.

Fraction	C_{po} (g/L)	k_1 (min^{-})^1	k_2 (min^{-1})	α
Hexoses	66,8	0,0405	9E-4	0,19
Pentoses	9,4	0,0448	1.4E-2	1,00

The kinetic model and experimental data for total hexoses and pentoses are shown in Figure 3. The models proposed for HMF and furfural are shown in Figure 4. The points represent the

experimental values, and the lines represent the model developed for each fraction of sugars. Even this is a simple model, it allows to describe suitably the solution and degradation products.

Sugar release occurs in a similar rate, as similar values of k_1 were obtained. However, pentoses decomposition to furfural is around ten times faster than hexoses decomposition (k_2 values).
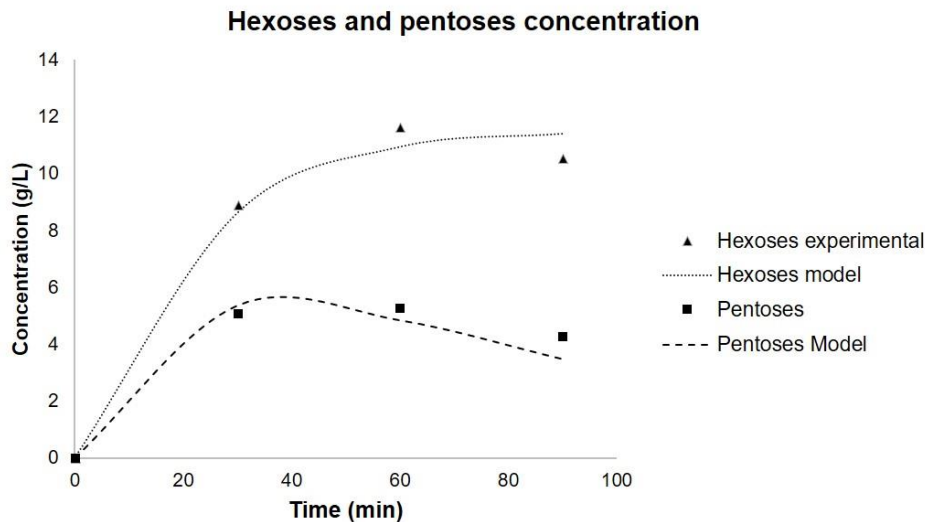

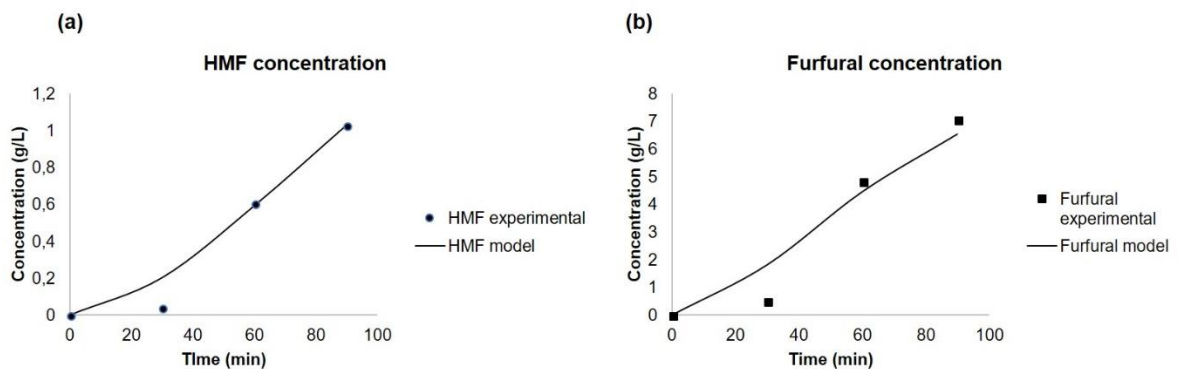**Figure 3: The kinetic curves for hexoses and pentoses of dilute acid treatment (without reuse).**

Figure 4: The kinetic curves for HMF and furfural of dilute acid treatment (without reuse).

When the liquor is re-used, the liquid media is expected to change, as it salts concentration, the ionic strength, the soluble organic compounds concentration is expected to increase. It is possible that sawdust deconstruction and degradation of sugars reaction rate could be affected by this. Also, undesirable humins could be formed. If the deconstruction rate remained unchanged with re-uses, the kinetic constants found in Table 2 has to adequately describe the evolution of components. In Figure 5 the estimated concentrations of hemicellulosic sugars and their degradation products in the spent liquor for re-uses 1 to 4 are shown.
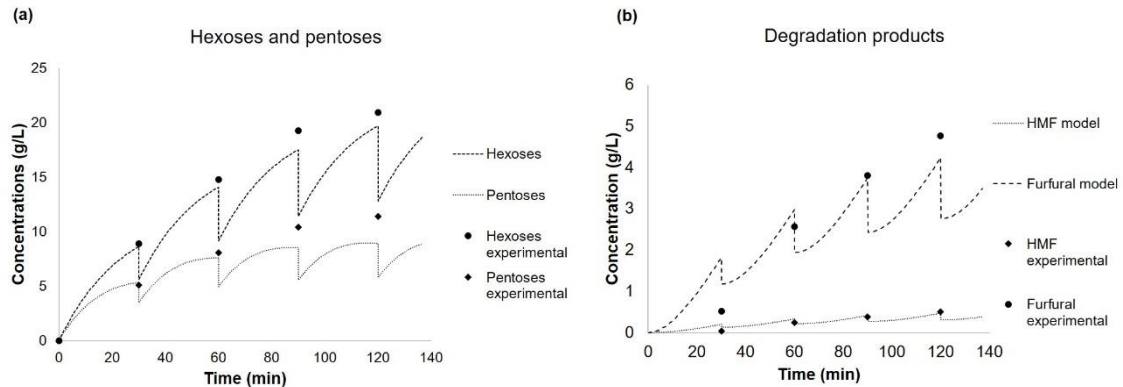
Figure 5: The kinetic model of the (a) concentrations hexoses and pentoses and (b) degradation products during the reuse of the spent liquor from dilute acid treatment.

The simulation shows a similar trend compared with experimental data. Slightly increase in sugar solubilization rate both for pentoses and hexoses is observed, as experimental points are higher than simulation results. More research is needed to explain this behavior. However, the difference between simulation and experimental results is less than 10%. This allows the use of this simulation with cost analysis purposes.

4. CONCLUSIONS

The reuse of the spent liquor increased significantly the total sugar concentration with the first and second reuse and after the third reuse, no significant changes in concentration were observed. Increase in the sugars concentration was mainly due to the hexoses contribution. The total sugars extracted in the four reuse was almost 33.4 g/L.

A simple kinetic evaluation for pine sawdust acid hydrolysis was conducted. From it, it can be shown that hexoses and pentoses are released at similar rate, and that pentoses are degraded ten times faster.

By simulating the re-cycle experiments with the kinetic model obtained from fresh diluted-acid data, it can be seen that the rate of sugar solubilization is reasonably described by the model, and enables the use of the model for cost analysis. Reactions rates seems to slightly increase with the re-used liquor.

No experimental problems were generated with the formation of humins.

The decision if this strategy is convenient or not, will be cost- based, considered in a biorefinery context. In this sense, pine sawdust can be separated in a valuable cellulose solid fraction and the spent liquor studied in this paper. More research is needed to evaluate the quality of the solid fraction, to consider the total cost of the process, as re-uses will significantly reduce it. The results obtained in this work allow to say that more than two re-cycles should not be useful if the product of interest are pentoses or its derived chemicals, as pentoses are strongly degraded. It could be useful for glucose- derived chemicals, and furfural or its derived chemicals.

The model will be used in a future work to perform an economic analysis in order to determine how much could be inferred in the total costs of the strategy proposed in the present work.

ACKNOWLEDGMENT

REFERENCES

1.   A. J. Ragauskas *et al.*, "The Path Forward for Biofuels and Biomaterials," *Science.*, vol. 311, num 80, pp. 484–489. (2006)
2.   Y.-H. P. Zhang, "Reviving the carbohydrate economy via multi-product lignocellulose biorefineries.," *J. Ind. Microbiol. Biotechnol.*, vol. 35, num. 5, pp. 367–75. (2008)
3.   J. A. Dumesic, D. M. Alonso, E. I. Gürbüz, and S. G. Wettstein, "Production of levulinic acid, furfural, and gamma valerolactone from C5 and C6 carbohydrates in mono- and biphasic systems using gamma- valerolactone as a solvent," US 2012/0302767 A1. (2012)
4.   S. W. Fitzpatrick, "Production of levulinic acid from carbohydrate-containing materials". (1997)
5.   J. Tanskanen, E. Rousu, J. Anttila, and P. Rousu, "Preparation of levulinic acid. FI Patent 20125274A". (2013)
6.   D. Datta, M. E. Marti, D. Pal, and S. Kumar, "Equilibrium Study on the Extraction of Levulinic Acid from Aqueous Solution with Aliquat 336 Dissolved in Di ff erent Diluents: Solvent's Polarity Effect and Column Design," pp. 6–13. (2016)
7.   Markets and Markets, "Formic Acid Market," 2017. [Online]. Available: https://www.marketsandmarkets.com. [Accessed: 10-Oct-2017].
8.   Allied Market Research, "Furfural Market Report," 2017. [Online]. Available: https://www.alliedmarketresearch.com. [Accessed: 11-Oct-2017].
9.   R. B. Stoffel, P. Vinholi, F. E. Felissia, L. Pereira, L. M. Gassa, and M. C. Area, "Hemicellulose extraction from slash pine sawdust by steam explosion with sulfuric acid," *Biomass and Bioenergy*, vol. 107, no. October 2016, pp. 93–101. (2017)
10. J. Sadhukhan, K. S. Ng, and E. Martinez, *Biorefineries and Chemical Processes: Design, Inntegration and Sustainability Analysis*, First Edit. United Kingdom: Wiley. (2014)
11. N. M. Clauser, M. E. Vallejos, and S. Gutiérrez, "Spent liquor reuse strategy applied to levulinic acid production," in *10th World Congress of Chemical Engineering(WCCE)*. (2017)
12. R. B. Stoffel, F. E. Felissia, A. A. Silva Curvelo, L. M. Gassa, and M. C. Area, "Optimization of sequential alkaline-acid fractionation of pine sawdust for a biorefinery," *Ind. Crops Prod.*, vol. 61, pp. 160–168. (2014)
13. R. B. Stoffel, "Fraccionamiento de aserrín de pino destinado a una biorrefinería forestal," Universidad Nacional de La Plata, Facultad de Ingeniería. http://sedici.unlp.edu.ar/handle/10915/52523. (2016)
14. Z. Chaula, M. Said, G. John, S. Manyele, and C. Mhilu, "Modelling the Suitability of Pine Sawdust for Energy Production via Biomass Steam Explosion," *Smart Grid Renew. Energy*, vol. 5, no. January, pp. 1–7. (2014)
15. S. Miller and R. Hester, "Concentrated Acid Conversion of Pine Sawdust to Sugars . Part II : High-Temperature Batch Reactor Kinetics of Pretreated Pine Sawdust," *Chem. Eng. Commun.*, vol. 194, no. December, pp. 103–116. (2007)
16. A. Rodríguez-Chong, J. A. Ramírez, G. Garrote, and M. Vázquez, "Hydrolysis of sugar cane bagasse using nitric acid: A kinetic assessment," *J. Food Eng.*, vol. 61, no. 2, pp. 143–152. (2004)
17. T. Tsoutsos and D. Bethanis, "Optimization of the dilute acid hydrolyzator for cellulose-to-bioethanol saccharification," *Energies*, vol. 4, no. 10, pp. 1601–1623. (2011)
18. R. Aguilar, J. a. Ramírez, G. Garrote, and M. Vázquez, "Kinetic study of the acid hydrolysis of sugar cane bagasse," *J. Food Eng.*, vol. 55, no. 4, pp. 309–318. (2002)