



Study of Liquor from Hemicelluloses Separation Process in Black Carob Tree Sawdust Biorefinery

Estudio del proceso de separación del licor de hemicelulosas en la biorrefinería de aserrín de algarrobo negro.

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Resumen

Este trabajo de investigación utilizó como materia prima aserrín de algarrobo negro pretratado, residuo abundante en la región del Nordeste Argentino y su objetivo fue optimizar la tercera etapa de un proceso de biorrefinería. El pretratamiento ácido en los procesos de biorrefinería se utilizó para extraer la máxima cantidad de hemicelulosas, retener la mayor concentración de celulosa en el sólido pretratado y evitar la degradación de los azúcares contenidos en el licor de proceso. Usando un diseño de experimentos central compuesto, se logró la optimización de la extracción de hemicelulosa de aserrín de algarrobo negro lavado

parcialmente deslignificado. Los resultados del diseño central compuesto, con dos repeticiones del punto central, han demostrado que es posible obtener licor con un rendimiento de 2,9 % de glucosa solubilizada, 54,5 % de xilosa solubilizada y 0,3 % de xilosa degradada, mediante un proceso óptimo utilizando 1,5 % de H₂SO₄, 7,7 % de sólidos durante 15,0 min.

Palabras claves: optimización, hemicelulosas, hidrólisis, aserrín algarrobo negro, biorrefinería.

Abstract

This research work utilized pretreated black carob tree sawdust as raw material, a vastly found waste in the Northeast Argentinian region and its objective was to optimize the third stage of a biorefinery process. The acid pretreatment in biorefinery processes was used to extract the maximum quantity of hemicelluloses, to retain the highest cellulose concentration in the pretreated solid and to prevent degradation of sugars contained in the process liquor. Using a central composite design of experiments optimization of hemicellulose extraction of partially-delignified washed black carob tree sawdust was achieved. Results from the central composite design of experiments, with two repetitions of the central point, have shown that it is possible to obtain liquor yielding 2.9% Solubilized glucose, 54.5% Solubilized xylose, and 0.3% degraded xylose, by an optimal process using 1.5% H₂SO₄, 7.7% solids for 15.0 min.

Keywords: optimization, hemicelluloses, hydrolysis, black carob tree sawdust, biorefinery.

Introduction

The growing interest in obtaining bio-based products, sustainable renewable energy, by using agro-industrial waste has encouraged research and development of processes for global biomass utilization. The core of chemical industry is the conversion of raw material into value-added products, including fuels, platform chemicals, polymers, pharmaceutical materials and products. Fossil resources have long been the main raw material for multiple chemical processes and transformations. However, sustainability has become a global must, due to significant depletion of fossil resources, and major scientific and political encouragement of the "biorefinery" paradigm as a solution for sustainable development. Biorefining consists of several sequential separation stages to extract different structural components of biomass. For biorefining, renewable raw material (biomass or food waste) is refined and/or improved to produce fuels and basic chemicals using chemical and biological conversion technologies (Esposito and Antonietti, 2015). Each type of treatment has a significant impact on upstream and downstream processes and are considered one of the costliest stages for biomass conversion.

Black carob tree (*Prosopis nigra*) is a South American leguminous tree species native to Gran Chaco Eco-region (particularly, the Chaco Húmedo and Chaco del Sudeste transition area), Argentina, Bolivia, Paraguay and Uruguay. It is known as black carob, sweet carob, purple carob and yellow carob. Plantation of black carob tree is abundant mainly in the province of Chaco (Argentina). The largest market for black carob tree is furniture and doors and windows, using 20-30% of tree wood, the remainder is waste used for different purposes. It is estimated that 28,000 tons of wood are processed monthly in Chaco, resulting in a daily waste production of 70 metric tons (Cuadra, 2012). This

residue could be processed to obtain bio-based products, adding value to simple open burning.

There is plenty of black carob tree sawdust in the Northeast Argentinian region, so its utilization and reclamation are of great interest, it is also a way to reduce pollution while obtaining products with greater added value. Black carob tree sawdust has been chemically processed in biorefineries, showing that it is possible to obtain water-soluble substances in the form of an aqueous solution, solid lignin of good quality and purity, and a solid rich in cellulose and hemicelluloses (Dagnino et al., 2020). This last solid can be treated with dilute acid to separate hemicelluloses in the form of sugars into aqueous solution, mainly xylose (Nitsos et al., 2016; Wang et al., 2015).

Hemicelluloses are the second most abundant polysaccharide in nature, following cellulose. Hemicellulose polymers can be converted into numerous by-products with different added values such as xylose syrup, furfural, xylitol, furan compounds and furan polymers, in biorefineries (Zhang, 2008). Among microbial co-products generated from hemicellulose sugars, xylitol is the most abundant and is used as food sweetener and moisture retention agent in pharmaceutical and cosmetic products (Winkelhausen and Kuzmanova, 1998; Villarreal et al., 2006). It is now widely used for products including toothpaste, gum, mouthwash, nasal spray (Clauser et al., 2016).

One of the most used treatments for hemicellulose extraction from lignocellulosic biomass is the dilute acid treatment, by which hemicelluloses can be dissolved and high xylose levels can be yielded, although it can include varied contents of furfural and hydroxy-methyl furfural (Jang et al., 2018). Therefore, hydrolyzed products must be studied and, in some cases, conditioned before evaluating possible applications of this fraction of lignocellulosic biomass.

In previous papers, acid treatment of washed black carob tree sawdust has been carried out with good results (Dagnino et al., 2013a). This treatment was also tested with other non-wood raw material (Dagnino et al., 2013b). In subsequent studies, it has been shown that lignin separation from hemicellulose-free washed black carob tree sawdust presented great difficulties (Dagnino et al., 2018); however, lignin extraction from washed black carob tree sawdust yields good results (Dagnino et al., 2020). Consequently, the objective of this research work is to optimize the third stage of black carob tree sawdust biorefinery process, that is, the optimization of hemicellulose extraction from partially-delignified washed black carob tree sawdust. It is important to mention that this optimization is part of the black carob sawdust biorefinery. Every stage focuses on the extraction of each of the components of interest without degrading, altering and/or losing another component of this raw material. Therefore, at this particular stage, hemicelluloses of good quality were extracted, avoiding damage cellulose by its hydrolysis. In summary, the extraction of hemicelluloses from partially-delignified washed black carob tree sawdust was optimized, minimizing its degradation, and preventing the solubilization and/or degradation of other components present in this raw material.

Material and Methods

Raw material

It Black carob tree (*Prosopis nigra*) sawdust (AAN, in Spanish aserrín de algarrobo negro) was supplied by a local industry in Resistencia, Chaco, Argentina. The size of raw material was determined by the feeding, rejection and sieving method, where the

material used passed through a 40-mesh screen but was retained by the 100-mesh screen. Then, water soluble extractives were separated by thoroughly washing the material with boiling deionized water, stirring it for two minutes, and filtering it using a 100 μ m sieve. The washed sample was dried at room temperature for 48h. The washed black carob tree sawdust (AANL, in Spanish aserrín de algarrobo negro lavado) was then processed in soda-ethanol-water to partially delignify the material. The optimal conditions of the delignification process were determined in a previous work (Dagnino et al., 2020). This preparation process is shown in the first four stages in Figure 1.

Partially-delignified washed black carob tree sawdust (AANLD, in Spanish aserrín de algarrobo negro lavado y deslignificado) was dried at room temperature for 48 hours, characterized following the techniques described in the section below and stored in a closed container at 4°C until later use.

Characterization of raw material and reaction products

Raw material: Raw material characterization included the determination of moisture content and/or volatile substances, according to NREL/TP-510-42621 standard. An analytical balance was used for the determination of moisture and volatile substances; water and ethanol-soluble extractive matter, according to NREL/TP 510-42621 standard, by quantification of extracted material on a dry matter basis using a Soxhlet extractor was conducted; content of carbohydrates, cellulose and hemicelluloses, according to the NREL/TP-510-42618 standard, by hydrolyzation of solid sample in two stages. The first stage consisted of 72% sulfuric acid solution at 30°C for 1 h. Secondly, it is diluted to 4% acid solution and autoclaved at 121°C for 1 h. For the liquid fraction, high-performance liquid chromatography (HPLC) on a Rezex™ RHM-Monosaccharide H + (8%) column (Phenomenex) is used to quantify structural carbohydrates according to the following chromatographic conditions: H₂SO₄ 5 mM as mobile phase, 0.6 ml/min, at 60°C and Refractive Index and UV detectors; content of lignin was determined, according to the NREL/TP-510-42618 standard, using the solid fraction of the method detailed in the previous step and using a muffle to calcine at 575 \pm 25°C for 2h.

Reaction Product: The treatment liquor was characterized by determination of sugar content (glucose, xylose, arabinose) and degradation products -organic acids (acetic acid), furfural and 5-hydroxy-methyl furfural (HMF). Quantification was carried out by HPLC, with a calibration curve based on the respective analytical standards at the same conditions as those described before.

Process optimization

The hemicellulose separation process was optimized by a central composite design of experiments (CCD) with two repetitions of the central point, using acid solution concentration (% H₂SO₄) solid content (% Sol, grams of AANLD in 100ml of solution) and reaction time (t) as independent variables. Table 1 shows the number of trials and the conditions under which were performed, according to the design of experiments. Results were analyzed by multivariate analysis of variance (ANOVA). Statgraphics software (Centurion XVI) was used for statistical analysis at a significance level of 95%.

| Trial # | H ₂ SO ₄ [%w/w] | % Sol | Time [Min] |
|---------|---------------------------------------|-------|------------|
| 1 | 1.80 | 7.50 | 15.00 |
| 2 | 1.00 | 3.30 | 15.00 |
| 3 | 1.50 | 10.00 | 20.00 |
| 4 | 1.50 | 5.00 | 20.00 |
| 5 | 0.50 | 5.00 | 20.00 |
| 6 | 0.16 | 7.50 | 15.00 |
| 7 | 1.50 | 5.00 | 10.00 |
| 8 | 1.00 | 7.50 | 23.40 |
| 9 | 0.50 | 10.00 | 10.00 |
| 10 | 1.00 | 7.50 | 6.60 |
| 11 | 0.50 | 10.00 | 20.00 |
| 12 | 0.50 | 5.00 | 10.00 |
| 13 | 1.50 | 10.00 | 10.00 |
| 14 | 1.00 | 11.70 | 15.00 |
| 15 | 1.00 | 7.50 | 15.00 |
| 16 | 1.00 | 7.50 | 15.00 |

Table 1. Trial Number, Conditions (H₂SO₄ % w/w, % solids, time in min) from CCD.

A 180ml capacity AISI316 stainless steel reactor was used for organic fractionation. Solid AANLD was mixed with the acid solution, then the reactor was closed and immersed in a silicone bath at 150°C for the specified time, without stirring. The reaction is stopped by cooling, placing the reactor in a water bath at 20°C. The liquid-solid mixture was then filtered through a 150-mesh sieve, the liquor was recovered, and pretreated solids were washed repeatedly with deionized water to remove the remaining solution.

Concentrations of glucose, xylose, and degradation products (i.e., furfural and 5-hydroxy-methylfurfural) were measured in the liquid fraction. Percentage of recovered solids was determined by the mass ratio of pretreated recovered solids to baseline raw material (dried weight pretreated material/dried weight of raw material).

Determination of degree of hydrolysis of cellulose and hemicellulose, percentage of solubilized glucose and xylose, was determined by glucose and xylose (calculated by HPLC analysis) mass ratio in process liquor and in baseline raw material (AANLD).

On the other hand, the degree of degraded xylose and glucose was quantified by mass ratio of glucose and xylose degraded in process liquor and baseline raw material (AANLD). The degraded glucose was calculated as the product of HMF concentration by the stoichiometric factor 1.4286 and degraded xylose was calculated as the product of furfural concentration by the stoichiometric factor 1.5625, both concentrations were calculated by HPLC analysis.

Flow diagram of black carob tree sawdust biorefinery can be seen in Figure 1.

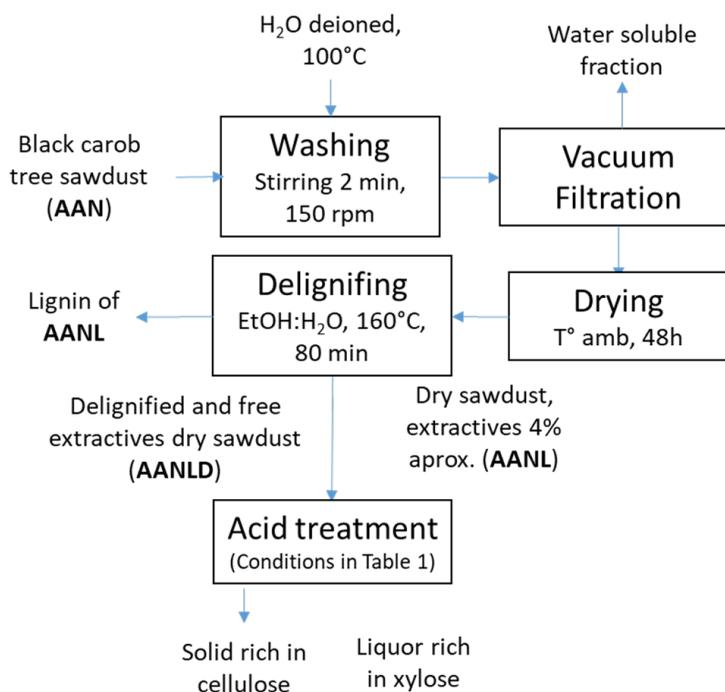


Fig. 1: Flow Diagram of Proposed Biorefinery Process for Black Carob Tree Sawdust.

Results and discussion

The raw material used was extractive-free partially delignified black carob tree sawdust. Characterization of this starting material stated that it is composed of 53.8% cellulose, 24.1% hemicelluloses, 22.0% lignin and is free of extractives. The raw material used differs from other hardwood used by other authors, for example, spruce sawdust contains a similar concentration of cellulose (55.4%), a lower concentration of hemicelluloses (5.6%) and a higher content of lignin (28.7%) (Alayoubi et al., 2020) and *Quercus mongolica* has lower concentration of cellulose and similar hemicellulose and lignin than AANLD (45.8% cellulose expressed as glucan, 18.6% hemicellulose expressed as xylan, 0.6% arabinan, 1.4% galactan plus 1.8% mannan and, 20.9% acid-insoluble lignin) (Jang et al., 2018). Although the various species of hardwood show certain differences in their composition, in this case, these differences are mainly due to AANLD being a treated material (washed and partially delignified).

AANLD ran different hydrolysis processes for hemicellulose separation, in black carob tree sawdust biorefinery, as shown in Figure 1. The objective of acid pretreatment in biorefinery processes is to extract the maximum quantity of hemicelluloses or to minimize hemicellulose residual concentrations in pretreated solids, to retain the highest cellulose concentration in pretreated solid material and to prevent degradation of sugars contained in the process liquor (Chadni et al., 2019).

Pretreatment with acidic solutions produces two products -i.e., enriched-cellulose solids and liquids containing sugars from hemicellulose hydrolysis, as well as small concentrations of their degradation products (furfural and 5-hydroxy-methylfurfural). The pretreated solid is raw material for numerous products, such as being hydrolyzed by cellulose enzymes,

producing glucose that is subsequently fermented for bioethanol production. While xylose can be used as raw material for products, including xylitol via fermentation. Consequently, an efficient pretreatment maximizes the cellulose content and minimizes the hemicellulose content in the pretreated solid, as well as maximizes the xylose content in the pretreatment liquor and prevents its degradation.

Study of process liquor

Table 2 shows the percentage of solubilized glucose and xylose, determined by glucose and xylose mass ratio in process liquor and in baseline raw material (AANLD), as well as the degree of degraded xylose and glucose, quantified by the mass ratio of the degraded glucose and degraded xylose in process liquor and in baseline raw material (AANLD).

The percentage of solubilized glucose is significantly lower than xylose as shown in Table 2. This is expected as the amorphous structure of hemicelluloses allows for greater reactivity against hydrolysis and, consequently, under the mild conditions used in this trial, hydrolysis is almost exclusively of hemicelluloses (Chadni et al., 2019). Therefore, glucose contained in liquor is mainly from hemicelluloses and it is not produced by cellulose hydrolysis (Banerjee et al., 2019). In addition, most hardwood contains approximately 5-10% easily hydrolyzable cellulose, which can be diluted acid concentrations below 1% v/v and under moderate temperatures (Vena et al., 2015).

The ANOVA analysis for the percentage of solubilized glucose variability shows that four effects have a p-value lower than 0.05, indicating they are significantly different from zero with a confidence level of 95.0%. The effects influencing the hydrolyzed glucose concentration are time ($p=0.0111$), sulfuric acid concentration squared ($p=0.0082$), mixture solid content squared ($p=0.0009$) and time squared ($p=0.0251$).

| Trial # | % SG | % SX | % DG | % DX |
|---------|------|------|------|------|
| 1 | 0.3 | 0.8 | 1.1 | 0.1 |
| 2 | 0.1 | 64.6 | 5.1 | 0.8 |
| 3 | 3.8 | 52.8 | 4.4 | 1.5 |
| 4 | 0.0 | 3.3 | 2.1 | 0.1 |
| 5 | 1.1 | 42.8 | 4.7 | 0.4 |
| 6 | 0.0 | 6.3 | 3.1 | 0.1 |
| 7 | 0.0 | 11.5 | 2.8 | 0.1 |
| 8 | 1.4 | 29.7 | 3.4 | 0.1 |
| 9 | 2.4 | 36.9 | 3.8 | 0.4 |
| 10 | 0.8 | 30.5 | 3.6 | 0.1 |
| 11 | 0.4 | 31.5 | 4.4 | 0.1 |
| 12 | 0.0 | 1.1 | 0.7 | 0.2 |
| 13 | 0.8 | 32.9 | 4.3 | 0.1 |
| 14 | 0.0 | 44.3 | 5.0 | 0.3 |
| 15 | 2.6 | 50.1 | 5.0 | 0.5 |
| 16 | 4.4 | 56.5 | 4.5 | 0.4 |

Table 2. Trial Number, Percentage of Solubilized Glucose (%SG) and Xylose (%SX), and Percentage of Degraded Glucose (%DG) and Xylose (%DX) Contained in the Process Liquor.

The R-Squared statistic indicates that the adjusted model translates into 74.2% variability in the percentage of solubilized glucose. Equation 1 of the adjusted model is:

$$\% \text{Solubilized glucose} = -30.92 + 10.70 * H_2SO_4 + 3.77 * \% \text{Sol} + 1.00 * t - 3.57(H_2SO_4)^2 - 0.20 * (\% \text{Sol})^2 - 0.03(t)^2 \quad (1)$$

Were:

t is the time;

H_2SO_4 is the sulfuric acid concentration;

% Sol is the mixture solid content.

As can be deduced from Eq. 1, the increase in significant variables causes an increase in the percentage of solubilized glucose up to a certain maximum value, after which it begins to decrease. This may be because increasing % H_2SO_4 decreases the activation energy of the hydrolysis reaction, in which the longer the reaction time, the greater the conversion and, the higher the solids content, the upper the availability. However, it is important to consider that, once the monosaccharide is obtained in solution, it is exposed to adverse conditions and can be dehydrated to HMF and other degradation products, reducing its concentration in the liquor. Accordingly, the estimated surface diagram (Figure 2) shows a concave function with maximum mean values for all three variables.

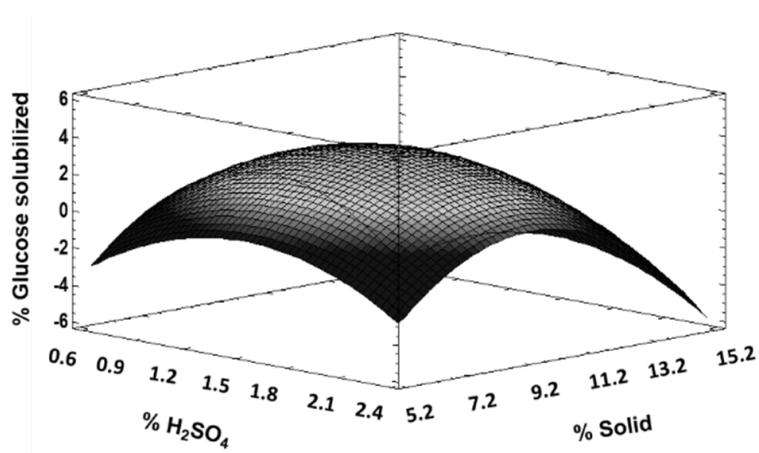


Fig. 2: Estimated Response Surface for the Percentage of Glucose Solubilized in the Process Liquor (reaction time was fixed at 15 min).

The optimization process of this acid pretreatment, aims at keeping % Solubilized glucose close to zero, thus the combination of variables keeping the percentage of solubilized glucose close to zero are: 1.7% H_2SO_4 , 11.7% Sol at 150°C for 7.7 min. To meet the objective, the system used relatively high concentrations of H_2SO_4 , but low levels of t and % Sol. Cai et al. reported glucose solubilization rates of 5.5% with some different reaction conditions (1% H_2SO_4 , at 117.5°C for 110.4 min) utilizing corncob as raw material (Cai et al., 2012).

The highest degree of solubilized xylose in the study range is 64.6%, in trial 2 (1% H_2SO_4 , 3.3% Sol for 20 min). According to the ANOVA analysis for the percentage of solubilized xylose variability, the influencing effects are content of solids ($p=0.0303$), time ($p=0.0000$), sulfuric acid concentration squared ($p=0.0116$), content of solids squared ($p=0.0294$) and

time squared ($p=0.0025$). Vena et al. have found that acid concentration, time and temperature are important factors in xylans extraction from *Eucalyptus grandis* being the highest extraction ratio 60.2% with 0.7% H_2SO_4 , at 140°C for 30 min (Vena et al., 2015). On the other hand, Jang et al. worked on the acid hydrolysis of *Quercus mongolica* (hardwood) autoclaved at 121°C, for 105 min 4% H_2SO_4 and obtained 83.0% hydrolysis of hemicelluloses. Also 12.6% of cellulose is hydrolysed, which indicates that a high xylose solubilization rate is accompanied by a degradation of cellulose, which is unfavourable in the context of a biorefinery (Jang et al., 2018).

The R-Squared statistic indicates that the adjusted model translates into 88.7% variability in the percentage of solubilized xylose. Equation 2 of the adjusted model is:

$$\% \text{Solubilized xylose} = -257.74 + 104.30 * H_2SO_4 + 19.42 * \%Sol + 216.93 * t - 34.77(H_2SO_4)^2 - 1.15 * (\%Sol)^2 - 0.45(t)^2 \quad (2)$$

Figure 3 shows the estimated response surface for the percentage of solubilized xylose in the process liquor. It can be seen a concave function with a mean value maximum for all three variables, the same behaviour as solubilized glucose (Figure 2). The function maximum can be explained by degradation reactions under severe conditions and insufficient hydrolysis under mild conditions (Chadni et al., 2019). Accordingly, under the most severe conditions, the highest proportion of degradation products (furfural and 5-hydroxy-methyl furfural) were observed. The xylose yield improves with an increase in the reaction time at the initial stages, but longer reaction times at high reaction temperatures easily cause the degradation of xylose to furfural (Liu et al., 2012).

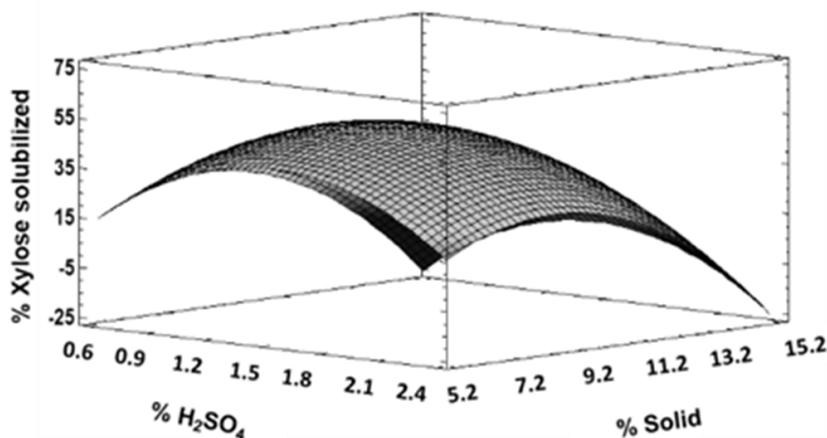


Fig. 3: Estimated Response Surface for the Percentage of Xylose Solubilized in the Process Liquor (reaction time was fixed at 15 min).

In pursuit of maximizing the hydrolysis of hemicelluloses, the optimal value for % Solubilized xylose is 74.1% and it is possible to reach this percentage in a process using 1.5% H_2SO_4 , 8.5% Sol for 18.8 min. Liu et al. performed kinetic studies of dilute acid hemicellulose hydrolysis, which concluded that xylose concentration increases with reaction time over a period, but it then begins to decrease due to its degradation to furfural (Liu et al. 2012). Such results are in line with the results obtained in this research. In addition, Kim et al. have

worked on a two-stage hydrolysis (alkaline-acid), the hydrolysis of hemicelluloses occurred in the second stage of 3% wt sulfuric acid solution, with yields of 71.7% under optimum conditions (130°C for 20 min) (Kim et al., 2011) and Guo et al. worked on the hydrolysis of Miscanthus (0.73% H₂SO₄, 150°C, for 6.1 min, 20% solid) and resulting in 66% of hemicellulose converted to xylose and 9% of furfural (Guo et al., 2012). On the other hand, some studies reached a hydrolysis of 90% and a low concentration of degradation products. These studies used relatively low temperatures, around 100°C, and a low solid load (4.8%), facilitating hydrolysis of hemicelluloses and favouring the accumulation of xylose (Jin et al., 2011).

Due to the process conditions, when hydrolysis of carbohydrates occurs, sugars are released. This sugars can degrade in contact with low pHs and relatively high temperatures. Glucose degrades to 5-hydroxy-methylfurfural and xylose degrades to furfural, by dehydration (Liu et al. 2012; Rafiqul and Sakinah, 2012). One of the objectives of the hemicellulose separation process is to protect or to reduce this degradation. To control this degradation process, the content of these products -5-hydroxy-methylfurfural and furfural- in the process liquor was measured. Table 2 shows the results in percentage of glucose and xylose degradation, respectively.

The ANOVA analysis on the variability of the glucose concentration degraded by process conditions stated that the exposure time increases glucose degradation, resulting in a significant variable with a p-value of 0.0000. While solid content and time squared decrease degradation, with p-values of 0.0051 and 0.0005, respectively.

The R-Squared statistic indicates that the adjusted model translates into 87.2% variability in the glucose concentration degraded to 5-hydroxy-methyl furfural. The regression Eq. 3 adjusted to study range data is as follows:

$$\% \text{glucose degradation} = -3.54 - 0.20 * \% \text{Sol} + 1.09 * t - 0.03 * (t)^2 \quad (3)$$

Figure 4 shows the estimated response surface for the glucose degradation concentration in the process liquor. As can be seen, by keeping an average time value of 15 min, the response of glucose degradation is linear.

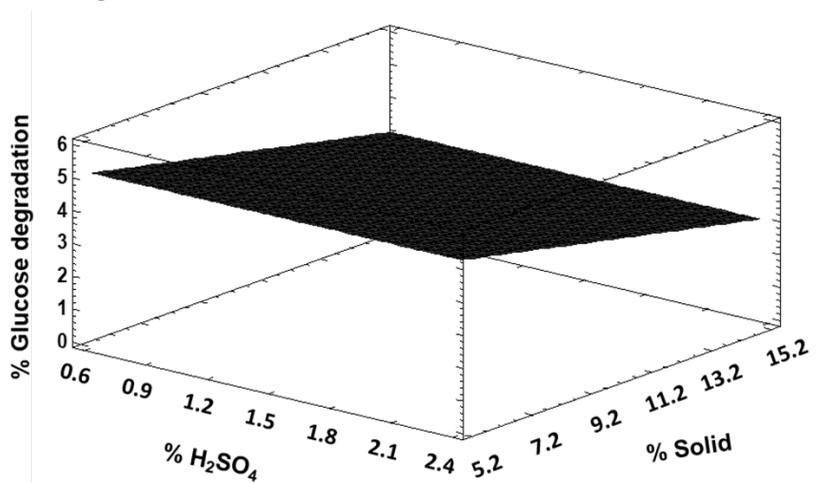


Fig. 4: Estimated Response Surface for the Grade of Glucose Degradation in the Process Liquor (reaction time was fixed at 15 min).

To obtain zero glucose degradation to 5-hydroxy-methylfurfural, the process should be run under the following conditions 1.7% H₂SO₄, 12.0% Sol for 6.7min.

Xylose concentration degrades because process conditions have a very similar behaviour to the glucose degradation process conditions. The ANOVA analysis shows that exposure time (p=0.0137) and solid content (p=0.0183) increase xylose degradation, while time variable-solid content interaction decreases degradation (p=0.0426).

The R-Squared statistic indicates that the adjusted model translates into 66.2% variability in the xylose concentration degraded to furfural. The regression Eq. 4 adjusted to study range data is as follows:

$$\% \text{xylose degradation} = -0.95 + 0.09 * \% \text{Sol} + 0.11 * t - 0.01 * \% \text{Sol} * t \quad (4)$$

Estimated response surface for the xylose degradation concentration in the process liquor is shown in Figure 5. As can be seen, by keeping an average time value of 15 min, the response of xylose degradation is linear as in the case of glucose degradation

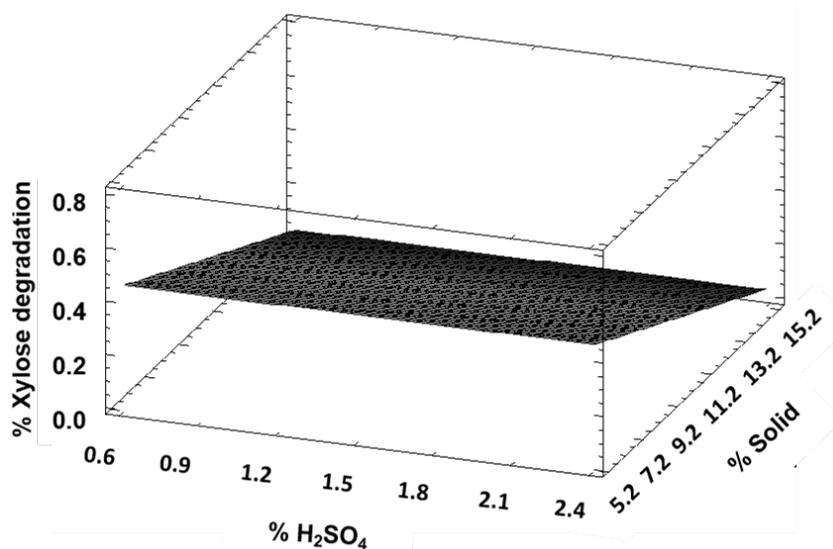


Fig. 5: Estimated Response Surface for the Grade of Xylose Degradation in the Process Liquor (reaction time was fixed at 15 min).

To obtain zero xylose degradation to furfural, the process should be run under the following conditions: 1.3% H₂SO₄, 6.9% Sol for 6.9 min. In other research, furfural yield was 1.6% of hemicellulose weight at 110°C for 120 min, while at 150°C for 120 min furfural yield reached approximately 15.8% (Liu et al. 2012). This result indicated that, a higher reaction temperature and shorter reaction time should be selected for hemicellulose hydrolysis in case of xylose degradation (Liu et al. 2012).

Optimization of separation of hemicellulose method

Desirability function was used for optimization of multiple responses. The variables considered in the optimization and its objective were the maximization of the hydrolyzed

xylose concentration and the minimization of the hydrolyzed glucose concentration and xylose degradation. Maximization of the grade of xylose solubilized present in the pre-treatment liquid was the most preponderant factor in response optimization, while glucose degradation was not necessary to be considered given it was minimized.

The estimated surface diagram for the desirability function obtained from the mentioned response variables is shown in Figure 6. This diagram was obtained using the Statgraphics software Multiple Response Optimization tool. This Figure shows that the optimal value does not appear under tested conditions (the desired function does not reach value 1). The highest value of the desirability function is 0.6. According to this model, optimal process uses 1.5% H_2SO_4 , 7.7% solids for 15.0 min. Several authors have worked on acid hydrolysis of hardwood, and optimal conditions from those papers differ from optimal conditions found in this research because initial pretreatments are different. For example, Guo et al. found as optimal condition a solution containing 0.73% H_2SO_4 (pH = 1.07), at 150°C for 6.1 min and 20% solids (Guo et al., 2012). Agreeing to Nistos et al. research, xylose recovery from process liquor reached 60% under moderate conditions (15% solids, at 170°C for 60 min) (Nistos et al., 2016). Liu et al. worked with sweet sorghum bagasse and obtained an ideal hydrolysis condition for xylose production with an acid solution of 3%, at 140°C for 50 min, with a xylose yield of 60% by weight, 12% glucose and 5.5% furfural (Liu et al., 2012).

According to the model, a 2.9% glucose solubilized, a 54.5% xylose solubilized, and a 0.3% degraded xylose liquor can be obtained under optimal pretreatment process conditions.

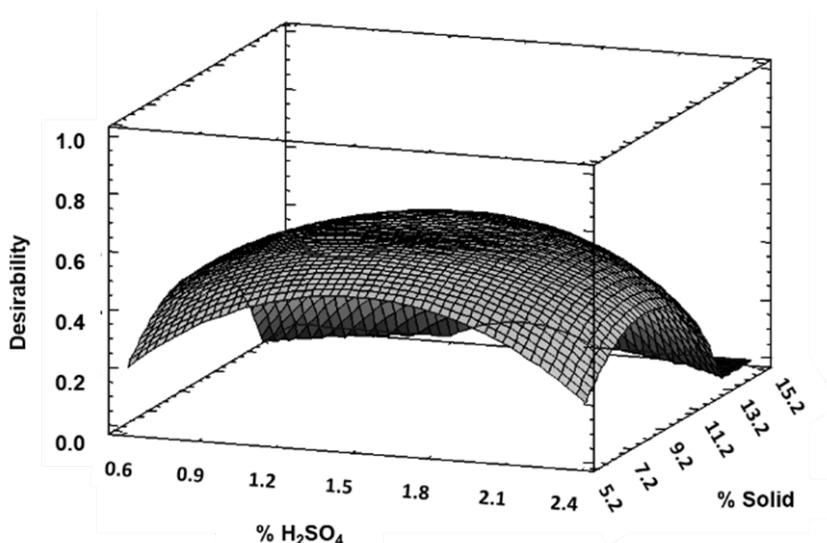


Fig. 6: Estimated Response Surface of the Desirability Function. Considering Maximization of the Percentage of Xylose Solubilized in the Process Liquor and, Minimization of Glucose and Xylose Degradation Products, (reaction time was fixed at 15 min).

Conclusion

The objective of the acid pretreatment in biorefinery processes was to extract the maximum quantity of hemicelluloses, to retain the highest cellulose concentration in the pretreated solid and to prevent degradation of sugars contained in the process liquor.

It was possible to optimize hemicellulose extraction from partially-delignified washed black carob tree sawdust by studying the process liquor. Results from central composite design of experiments, with two repetitions of the central point have shown that it is possible to obtain 2.9% glucose solubilized, 54.5% xylose solubilized, and 0.3% degraded xylose by running an optimal process using 1.5% H₂SO₄, 7.7% solids for 15.0 min.

Combination of variables preventing cellulose hydrolysis were: 1.7% acid concentration, 11.7% solid content at 150°C for 7.7 min. Under these optimal process conditions, percentage of glucose solubilized would be close to zero.

The optimal value for the percentage of xylose solubilized is 74.1% and it is possible to reach this percentage in a process using 1.5% H₂SO₄, 8.5% Sol for 18.8 min.

In order that glucose degradation to 5-hydroxy-methyl furfural is close to zero, the process should be run under the following conditions 1.7% H₂SO₄, 12.0% Sol for 6.7 min. Considering the same objective as xylose degradation to furfural, the process should be run under the following conditions 1.3% H₂SO₄, 6.9% Sol for 6.9 min.

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