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FERMENTABLE SUGARS FROM EUCALYPTUS GLOBULUS: PROCESS OPTIMIZATION

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ABSTRACT: In the last years, The production of bioethanol from lignocellulosic materials is having more attention from the researchers due to the abundance of this raw material in certain regions, it is cheaper, does not compete with foods like sugarcane or corn, and can reduce up to to 86% of carbon dioxide emissions when is compared with gasoline. However, the process economy is linked to the pretreatment needed to make accessible the cellulose for further steps of enzymatic hydrolysis and fermentation. Then, the motivation of this work is propose a MILP model to perform an optimal synthesis of the pretreatment for obtain fermentable sugars from the Eucalyptus globulus specie. For this purpose, a General Disjunctive Program (GDP) is formulated. The results obtained suggest that difference between a two-step pretreatment process (pretreatment with posthydrolysis) against just one pretreatment step of Diluted Acid process is small.

Highligths

- Pretreatment process for bioethanol production from lignocellulosic materials.
- Termochemical pretreatment and posthydrolysis process.
- Process Synthesis.
- Generalized Disjunctive Programming model.

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ABSTRACT: In the last years, bioethanol production from lignocellulosic materials is receiving more attention from researchers since it is an abundant raw material in certain regions, it is cheaper, does not compete with foods like sugarcane or corn, and can reduce up to 86% of carbon dioxide emissions when compared with gasoline. However, the process economy is linked to the pretreatment needed to make the cellulose accessible for further steps of enzymatic hydrolysis and fermentation. Then, the motivation of this work is to propose a MILP model to perform an optimal synthesis of the pretreatment for obtaining fermentable sugars from the *Eucalyptus globulus* specie. For this purpose, a General Disjunctive Program (GDP) is formulated. The obtained results suggest there is a small difference between a two-step pretreatment process (pretreatment with posthydrolysis) and one-step pretreatment of Diluted Acid process.

1. Introduction

Research in biofuels production has increased in the last decade due to the growth in the energy demand, the uncertainty in the amount of fossil reserves and the environmental issues that arise in relation to the use of fossil fuels. Among different biofuels, ethanol is an important one because it is produced in several countries using different raw materials: sugarcane in Brasil and corn in the United States of America. They are both massive producers, totalizing a 90% of the world production that was 65.3 millions of cubic meters in 2008 (Machado 2010), and 75.1 million in 2011 (Amarasekara 2014). Biofuels from sugarcane and corn are widely criticized because they compete with food production. This is the reason for seeking alternative raw materials, in particular lignocellulosic ones. In the work by (Yue et al. 2014), the authors mention that lignocellulosic and algae-based biofuels have advantages over first-generation biofuels as regards the implications in food prices and land competition. Čuček et al. 2014 developed a generic mathematical model that can be used for analyzing of the optimal utilization of raw materials, production processes, and products, in any biomass supply chain network, incorporating recycling and heat integration. Similarly, Miret et al. 2015, presented a Mixed Integer Linear Program (MILP) in which economic, environmental, and social dimensions are included. As a result of this multi-objective model, they observed that wood-based fuels have advantages over corn-based as regards the economic and environmental dimensions. In the work by (Drigo et al. 2009), the amount of sawmill wastes in Argentina is reported to be about 1,700 annual tons without including the waste produced from forest harvesting, which could also represent an important amount. Considering residuals from sugarcane and other agricultural exploitations together with those previously mentioned, the amount of lignocellulosic materials would be around 3,2

million of annual tons. Even with a conservative conversion, that amount would yield about 600 thousand tons of ethanol per year, an important quantity that cannot be ignored. By the Energy Independence and Security Act of 2007, USA sets annual targets for biofuels production from lignocellulosic materials from 2010-2022 to reach 47.8 million tons by 2022. Some studies indicate that the use of ethanol produced from lignocellulosic materials is associated with a balance of carbon dioxide that is 86% lower than gasoline and 82% lower than the use of ethanol obtained from corn (M. Wang et al. 2007).

The obtention of fermentable sugars from corn and sugarcane is relatively easy but it is not the case when talking about lignocellulosic materials because a pretreatment process is needed to decompose the polysaccharides that form celluloses and hemicelluloses, which form the cell wall. Although there have been several experiments to decompose lignocellulosic material without previous treatments, the results show a very low yield in the production of fermentable monosaccharides. This is due to the existence of a wall of hemicellulose and lignin which protect the cellulose microfibers. To overcome this obstacle, at least a partial decomposition of those materials is required (Bhaskar et al. 2011). Several pretreatment processes exist but the most studied one is the thermochemical one. The acid process has a high level of maturity. It was studied during the second world war (K. Wang and Sun 2010).There are several variants of this process but the dilute acid is the most promising one. In recent years, the Autohydrolysis (hot liquid water) and Steam Explosion processes have become more relevant.

A work by Zaldivar describes the proposed current process for the production of ethanol from lignocellulosic materials rich in pentose (Zaldivar et al. 2001). This process starts by acid hydrolysis, followed by liquid-solid separation and washing. The liquid phase is subsequently detoxified and pentose fermentation is performed while the solid phase is enzymatically hydrolyzed and the produced hexoses are then fermented. The lignin remaining (solid) is separated and used to generate the required energy. They also mention the efforts to integrate and simplify the process. In the article by (Cardona et al. 2010), a review of the various processes that have been studied for the production of ethanol from sugar cane is presented. They also present a general outline of each studied technology within the corresponding processing steps. In both descriptions, it is considered that the fermentation of the liquid stream may be perform after detoxification, while in cases of Autohydrolysis and Steam Explosion it is also recommended to carry out a second hydrolysis process to the liquid phase for obtaining a greater amount of monosaccharides. This also enables the use of less severe pretreatment conditions, decreasing the formation of furfural and 5-hydroximethyl-2-furfural (HMF) (Duarte et al. 2009; Guo 2012; Wyman 2013).

Ethanol production processes present differences according to the cellulosic raw material depending on the hardness or softness of wood, the difference being based on the hemicellulose composition. In the case of hardwoods and other xylose-rich species, the fermentation step involve a greater challenge than that for softwoods. Hardwoods imply the fermentation of pentoses, which is a more complex process than fermentation of hexoses, although there have been many advances in recent decades (Antunes et al. 2014; Kuhad et al. 2011; Mishra and Singh 1993; Zaldivar et al. 2001). In recent years,

great emphasis has been placed on the development of simultaneous fermentation of hexoses and pentoses (or co-fermentation). This technology involves major challenges (Stambuk et al. 2008), but several advances have occurred through genetic modification of microorganisms, such as the *Zymomonas mobilis* bacteria (Mohagheghi et al. 2002), *Saccharomyses cerevisiae* yeast (Erdei et al. 2013; Ishola et al. 2015; Ohgren et al. 2006) and *Escherichia coli* bacteria (Takahashi et al. 2000). In this sense, some advances were made by co-culture of microorganisms (Fu et al. 2009; Mishra and Singh 1993). The work by (Dutta et al. 2010) compare different configurations for fermented saccharides that are presented in corn stover (an xylose-rich material). The microorganisms used are *S. cerevisiae* and genetically modified *Z. mobilis.* The find that the most economical arrangement is separate fermentation of cellulose-rich solid and the hydrolyzate streams.

Two simplified flowsheet alternatives for the process of ethanol obtention from lignocellulosic materials are shown in Fig 1. The schema of Fig. 1-a is adequate for xylose-rich materials, such as hardwoods, due to the complexity of performing a co-fermentation stage. The liquid stream after pretreatment is mainly composed of pentoses and that is why a separate fermentation must follow. On the other hand, the flowsheet of Fig. 1-b is adequate for softwoods, because the liquid downstream after the pretreatment step is mainly composed of hexoses, so that this stream can be fermented together with the effluent of the cellulose enzymatic hydrolysis.
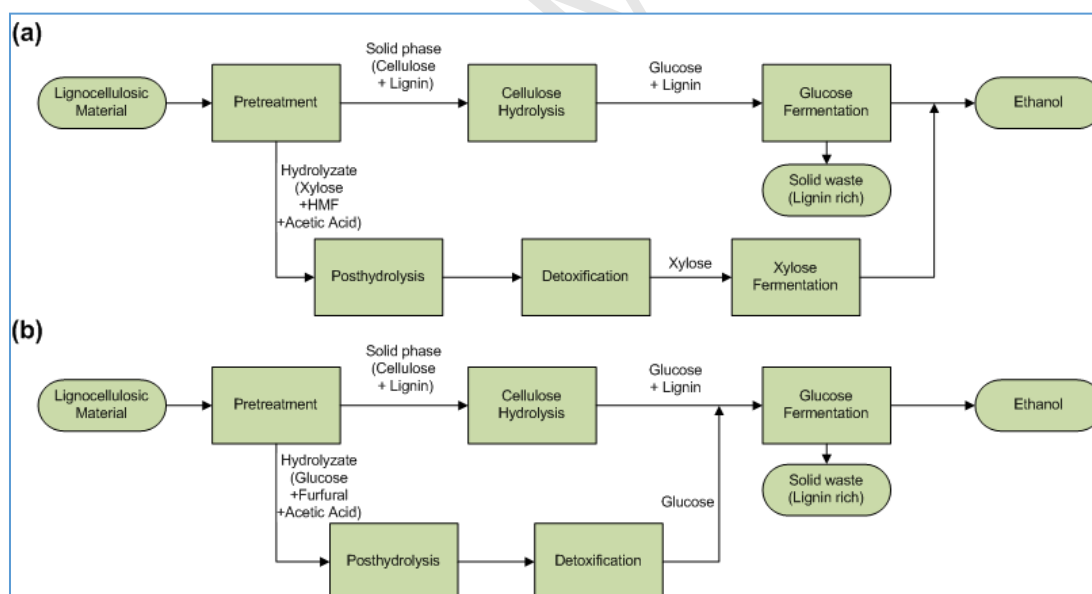

Fig. 1: Process of ethanol obtention from hardwoods (a) and softwoods (b).

In general, the agricultural waste like sugarcane bagasse, corn stover, cotton stalk, tobacco stalk, sunflower stalk, or cereal straws have a hemicellulose composition similar to hardwoods (Akpinar et al. 2009; Amarasekara 2014), since all of them comes from the Angiosperm's family. Since the amount of agricultural waste and hardwoods is abundant, the study in this work is focused on this type of raw material, especially on the *Eucalyptus globulus* species because this particular tree grows easily and has several advantages, like the size and weight of the trees and that the plantation area was increased in the last

two decades. The composition of *E. globule* is 39.9% cellulose, 0.7% glucan, 14.9% xylan, 2.3% acetyl groups and 28.4% lignin, according to Gütsch et al. (2012).

Many experimental works search the operating conditions that improve the process for different combinations of raw materials and pretreatments. These works have different optimization criteria, which are mainly the maximization of glucose and xylose recovery or the enzymatic digestibility of cellulose (Boussarsar et al. 2009; Canettieri et al. 2007; Canilha et al. 2011; Martin-Sampedro et al. 2014; Nitsos et al. 2013; Romaní et al. 2010a). Also, there are several works in the literature, dealing with pretreatments to decompose hemicellulose and lignin (which are barriers for the enzymatic hydrolysis) and, at the same time, maintaining a major content of cellulose in the solid phase (Gütsch et al. 2012; Romaní et al. 2012; Romaní et al. 2013). A smaller number of studies have sought, experimentally, favorable conditions for the pretreatment of lignocellulosic materials and a low amount of reactions inhibitors in the steps following the pretreatment process. The work by (Abril et al. 2012) addresses the hydrolysis of sugar cane bagasse by Autohydrolysis using a factorial design 3^2. They search high solubilization of xylose (> 35 g/L), low levels of furan and phenol (<2.5 g/l and <1.5 g/l respectively), and a limited value of the percentage of hemicellulose in the solid phase (<3%). As a result, they found that the goals are achievable with working temperature being between 180 ºC and 190 ºC and a processing time of 60 to 82 minutes. A similar work is found in (Dagnino et al. 2013). They performed an experimental exploration of the operating conditions in dilute acid hydrolysis of rice husks by applying a Response Surface Methodology (RSM). Their aim is to find the combination of temperature, acid concentration, and treatment time to maximize the xylose content in the liquid phase, cellulose in solid phase and minimize the hemicellulose in solid phase while maintaining a low formation of HMF and furfural. To perform the optimization of multiple objectives, different desirability functions are used.

The ethanol production process using lignocellosic materials has been studied by several works of the area of Process Systems Engineering. Various models of simulation, optimization and synthesis, have been proposed. The work by Conde-Mejía et al. (2012) made a comparison of thermochemical pretreatments respect to the cost of energy and chemicals used. They performed several Aspen-Plus simulations based on parameters of conversion yields and stoichiometric ratios. It was found that processes of Steam Explosion, Autohydrolysis, dilute acid and ammonia fiber explosion are those with lower cost per ton of dry biomass. In a later work of the same authors (Conde-Mejía et al. 2013), these four thermochemical pretreatments with different configurations of cellulose hydrolysis and fermentation are studied. Several Aspen-Plus simulations are performed. The authors conclude that the lowest cost of ethanol production is obtained by a dilute acid pretreatment, followed by a separate saccharificacion of cellulose and co-fermentation of hexoses and pentoses. In the article by Martín and Grossmann (2012), a superstructure that covers all stages of bioethanol production from switchgrass is developed. The work includes the ammonium fiber explosion (AFEX) and the dilute acid process, as possible pretreatments; the enzymatic hydrolysis followed by co-fermentation; and distillation, adsorption corn-meal, molecular sieves and pervaporation as alternatives for the ethanol purification stage. The authors conclude that the optimum configuration from the economic point of view includes the use of acid pretreatment and a combination of distillation with molecular sieves for ethanol separation. In the work by Furlan et al. (2012), the authors proposed a simulation and optimization model of a plant that integrates the production of

first- and second-generation ethanol from sugarcane. The model decides on the proportion of bagasse which is intended for the production of second-generation ethanol, subject to the constraint of energy self-sufficiency of the overall process. The aim is to maximize an economic function that includes sales revenue of ethanol, electricity, yeast, and bagasse, as well as the costs of enzymes and sugarcane. The optimization is performed by the particle swarm optimization method (PSO). In all the above mentioned works, the pretreatment stages are modeled by parameters of conversion yields obtained from the literature.

Also, some works of mathematical modeling of the pretreatment steps have been found. Ramirez and Fraga (2009) propose a nonlinear programming model (NLP) for the hydrolysis by dilute acid. This is applied to the case of bagasse sugarcane. Genetic algorithm is used to optimize process conditions (temperature, solid-liquid ratio, residence time, and acid concentration). The aim is to maximize the final glucose concentration. In the work by López-Arenas et al. (2013), a mathematical model has been proposed to maximize the speed of xylose through a process with dilute acid, using sugarcane bagasse as raw material. A continuous reactor is modeled with a fixed time of residence, while the acid concentration, the temperature and the solid-liquid ratio are changed. The optimization is performed by analytical methods. They find that temperature is the most influential factor while acid concentration is the second one.

The objective of this work is to perform the synthesis of the pretreatment step for *E. globulus*, in combination with the posthydrolysis stage, including the reaction kinetics, in order to maximize the fermentable sugars while limiting the inhibitors concentration. According to our knowledge, there no exists works in the open literature that deal with this problem. For this purpose, it has developed a mixed integer linear problem (MILP), which includes the kinetics of decomposition processes. The synthesis of the process is performed considering various amounts of cellulose recovery. The results of the combination of pretreatment and posthydrolysis are also compared with the case of using only a dilute acid pretreatment, under optimal operating conditions. The results obtained are shown in section 5.

2. **Kinetic reactions of wood decomposition in termochemical process**

The goal of the thermochemical pretreatment processes is to increase the accessibility to the cellulose contained in the wood by the selective decomposition of the hemicellulose and lignin. In this step, the task is to cut the polymers and liberate into the liquid phase xylo-oligosaccharides, gluco-oligosaccharides, xylose, glucose and acetic acid. At the same time, are produced some undesirable decomposition products like furfural and HMF. These components together with acetic acid are strong inhibitors in the alcoholic fermentation step (Delgenes et al. 1996). For the case of furfural and HMF the concentration depends on the operating conditions of the treatment, while the acetic acid is liberated during the hemicellulose hydrolysis independently of the process conditions. This situation makes that after the pretreatment a detoxification step for the acetic acid is needed.

The components that can be fermented by using microorganisms are glucose and xylose, therefore, the goal is to maximize the obtaining of these species while minimizing the amount of inhibitors. For this purpose, it is needed a kinetic model of the main reactions including the decomposition ones. First order kinetics has been used successfully in several works to model the reactions of decomposition process in the pretreatment steps (Aguilar et al. 2002; Conner and Lorenz 1986; Garroteet al. 1999, 2001; Lavarack et al. 2002; Moreno et al. 2013; Sales-Cruz et al. 2011). Such reactions can be represented by a system of differential equations of the first order, which is expressed in Eq. (1). C is the vector of the concentrations of soluble compounds at a given time (in grams per gram of water). In the case of solid components, they are assumed that are solubilized. K is the coefficient matrix representing the decomposition rates and formation of the components.

$$\frac{dC}{dt} = K \cdot C \tag{1}$$

Multiplying both sides of the Eq. 1 by the amount of process water, it is obtained the equation Eq. (2). This define the relationships among the components amount in the reactor during the wood decomposition reactions; where m is the vector representing the components amounts.

$$\frac{dm}{dt} = K \cdot m \tag{2}$$

In Eq. (3) and (4) the elements of vector m and matrix K are shown. CR_n is the conversion relationship of the components obtained from the n compound of vector m, while k_n is the decomposition velocity of that compound, which depends on the pretreatment and the operating conditions.

$$m = \begin{pmatrix} m_{cellulose} \\ m_{glucan} \\ m_{xylan} \\ m_{acetyl\,group} \\ m_{oligo-glucose} \\ m_{oligo-xylose} \\ m_{glucose} \\ m_{xylose} \\ m_{HMF} \\ m_{furfural} \\ m_{acetic\,acid} \\ m_{lignin} \end{pmatrix} \tag{3}$$

$$K = \begin{bmatrix} -k_1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & -k_2 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & -k_3 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -k_4 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ CR_1 \cdot k_1 & \cdot & \cdot & \cdot & -k_5 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & CR_3 \cdot k_3 & \cdot & \cdot & -k_6 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & CR_2 \cdot k_2 & \cdot & \cdot & CR_5 \cdot k_5 & \cdot & -k_7 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & CR_6 \cdot k_6 & \cdot & -k_8 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & CR_7 \cdot k_7 & \cdot & -k_9 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & CR_8 \cdot k_8 & \cdot & -k_{10} & \cdot & \cdot \\ \cdot & \cdot & \cdot & CR_4 \cdot k_4 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -k_{12} \end{bmatrix} \quad (4)$$

3. Superstructure and problem definition

In Fig. 2, it is presented the superstructure proposed with the selected treatments to be synthesized using *E. globulus* as raw material. Although it is a simple scheme, it has been included to clarify the alternatives in the initial stage of the process.

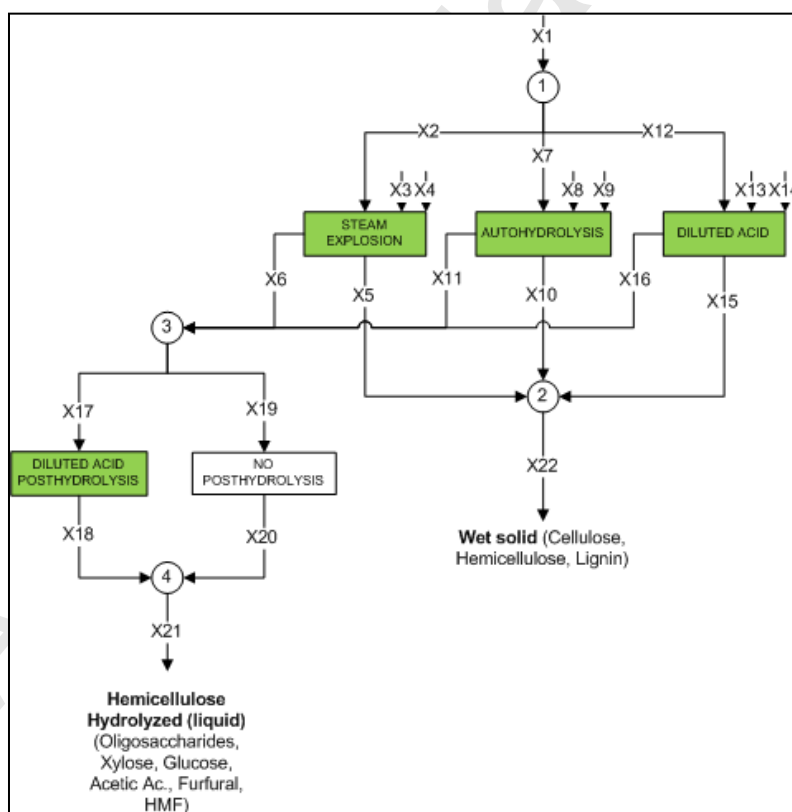**Fig. 2:** Superestructure of pretreatment y posthydrolysis process.

The objective is to select a process with a high yield in the extraction of polysaccharide from wood. For this purpose, it is posed a multi-objective problem to maximize the xylose amount in the hydrolyzed stream and the amount of cellulose in the solid-phase, which is hydrolyzed through enzymatic methods that are more selective than

the thermochemical ones. The constraints are the mass balances, the kinetic of the decomposition chemical reactions, and the maximum concentrations of HMF and furfural of the hydrolyzed stream. The decision variables of the model are: the selection of the pretreatment process, if a posthydrolysis stage is needed, as well as the operation conditions like temperature, processing time and catalyzer concentration, which have influence over the kinetic of the decomposition reactions. Such conditions have been discretized to obtain a Mixed Integer Linear Program (MILP) model.

4. **Mathematical model**

The problem is multi-objective where the functions to be maximized are the xylose content in the hydrolysis stream and the cellulose in the solid stream, which are expressed in Eq. (5) and Eq. (6) respectively.

$$fobj1 = f_{21,Xylose} \tag{5}$$

$$fobj2 = f_{22,Cellulose} \tag{6}$$

In order to solve the problem the ε-constraint methodology was used to determine the Pareto curve covering both objective functions. This method is preferred to goal programming because it is easier to set limits to the domain of interest. Additionally the goal programming could present the disadvantage that the same solution can be obtained for different combinations of weights in the objective function, making it difficult to obtain the Pareto curve (Mavrotas 2009). Eq. (7) establishes the minimum amount of cellulose that can remain in the solid phase after pretreatment, where ε can take the value between 0 and 1.

$$f_{22,Cellulose} \geq \varepsilon \cdot f_{1,Cellulose} \tag{7}$$

Eq. (8) limits the inhibitors compounds concentration in the hydrolyzed for fermentation purposes. *Inhib* represents the set of inhibitors compounds and *MaxCon* is the maximum concentration of these, in hydrolizate stream.

$$f_{21,c} \leq MaxCon_c \cdot f_{21,LiqWater} \qquad \forall c \in Inhib \tag{8}$$

Eq. (9) establishes the input flow for each component in the pretreatment process, where *C* is the set of species to consider in the model, *Productivity* is the amount of dry wood entering into the process and *RMComp* is the amount of each component per unit of dry wood.

$$f_{1,c} = RMComp_c \cdot Productivity \qquad \forall c \in C \tag{9}$$

Eq. (10), (11) and (12) define the flow of solids, solutes and water (solvents) respectively, on each stream j. This distinction is made because the proportions between solid, solute and solvent in the output of pretreatment processes depend on the conditions of these processes. This in turn affects the subsequent washing steps and phase separation, as well as the concentrations of the inhibitory compounds.

$$F_j^{Sld} = \sum_{c \in Sld} f_{j,c} \qquad \forall j \in J \tag{10}$$

$$F_j^{Slt} = \sum_{c \in Slt} f_{j,c} \qquad \forall j \in J \tag{11}$$

$$F_j^{Slv} = \sum_{c \in Slv} f_{j,c} \qquad \forall j \in J \tag{12}$$

Eq. (13) is the total flow for each stream *j*.

$$F_j^{Tot} = F_j^{Sld} + F_j^{Slt} + F_j^{Slv} \quad \forall j \in J \tag{13}$$

Eq. (14) corresponds to the material balances for each node *n* of the superstructure and each component *c∈ C*.

$$\sum_{j \in NodIN_{nd}} f_{j,c} = \sum_{j' \in NodOUT_{nd}} f_{j',c} \quad \forall nd \in ND, c \in C \tag{14}$$

The Eq. (15) and (16) fix the water flow of the washing stream and process stream, respectively according to the lignocellulosic material that enters into the process. *WSRPrt* and *WSRWash* are the water/solid relationship for the pretreatment and the washing, respectively; *WaPrcIN*, *WaWashIN*, *ProdPrcIN* are the input set for the process and washing water and the lignocellulosic product for each treatment, respectively. It has been assumed that in the washing step, all soluble compounds are dragged into the liquid and are added to the hydrolysis stream. *Prc* is set of process modeled in this work {SE=Steam Explosion, AH=Autohydrolysis, DA=Diluted Acid, DAP=Diluted Acid Posthydrolysis, NP=No Posthydrolysis}, and *Prt* is the subset of pretreatments {SE, AH, DA}.

$$F_j^{slv} = WSRPrt_{prc} \cdot F_{j'}^{Sld} \quad \forall prc \in Prt, j \in WaPrcIN, j' \in ProdPrcIN \tag{15}$$

$$F_j^{slv} = WSRWash_{prc} \cdot F_{j'}^{Sld} \quad \forall prc \in Prt, j \in WaWashIN, j' \in ProdPrcIN \tag{16}$$

Eq. (17) is to determine the water flow in the solids coming from the washing step.

$$F_j^{slv} = HOutWash_{prc} \cdot F_j^{sld} \qquad \forall prc \in Prt, j \in ProdPrcOUT \tag{17}$$

Eq. (18) set up the water balance for each process *prc* belonging to the set of pretreatments *Prt*, where *PIN* and *POUT* are the sets of input and output streams respectively, *StLoss* is the steam lost flow, which is greater than zero for the Steam Explosion Process. This flow is determined in Eq. (19) where *SteamExp* is the amount of steam per unit of lignocellulosic material that enters into the process.

$$\sum_{j \in PIN_{prc}} F_j^{slv} = \sum_{j' \in POUT_{prc}} F_{j'}^{slv} + StLoss_{prc} \qquad \forall prc \in Prt \tag{18}$$

$$StLoss_{prc} = SteamExp_{prc} \cdot \sum_{j \in PrcIN_{prc}} Fsld_j \qquad \forall prc \in Prt, \tag{19}$$

Eq. (20) set to 0 the flows *j* of the components *c* which do not belongs to the set *JC*.

$$f_{j,c} = 0 \qquad \forall (j,c) \notin JC \qquad (20)$$

In Eq. (21) the set of decisions about the type of pretratments and operating conditions is established. This is accomplished through embedded disjunctions. Observe that a set of binary variables that select the operating conditions and the type of process to be used are defined. The binary variable Y_{prc} is set to 1 when the process prc is selected and is equal to 0 otherwise. La variable $U_{prc,p}$ is activated when the prc process is selected with a duration of tp_p. The variable $W_{prc,p,t,a}$ is equal to 1 when are selected the prc treatment , with a duration of tp_p, temperature T_t and the catalyzer concentration of A_a.

$$
\begin{bmatrix}
Y_{prc} \\[4pt]
\begin{bmatrix}
\underset{p \in P}{\vee}
\begin{bmatrix}
U_{prc,p} \\[4pt]
m^{t0}{}_{prc,c} = tp_p \cdot \sum_{j \in PIN} f_{j,c} \qquad (20.1) \\[4pt]
m^{tf}{}_{prc,c} = tp_p \cdot f_{j,c} \quad \forall j \in ProdPrcOut; c \in Sld \quad (20.2) \\[4pt]
m^{tf}{}_{prc,c} = tp_p \cdot f_{j,c} \quad \forall j \in HydrPrcOut; c \in Slt \quad (20.3) \\[4pt]
\underset{\substack{t \in T \\ a \in A}}{\vee}
\begin{bmatrix}
W_{prc,p,t,a} \\[4pt]
m_{1,c} = m^{t0}{}_{prc,c} \qquad \forall c \in (Sld \cup Slt) \quad (20.4) \\[4pt]
\dfrac{m_{i+1,c}}{\Delta t_p} - \dfrac{m_{n,c}}{\Delta t_p} - \dfrac{1}{2} \cdot \sum_{c'} K_{prc,c,c',t,a} \cdot m_{i,c'} \\
\quad - \dfrac{1}{2} \cdot \sum_{c'} m_{prc,c,c',t,a} \cdot m_{i+1,c'} = 0 \quad \forall i, c \in (Sld \cup Slt) \quad (20.5) \\[4pt]
m_{if,c} = m^{tf}{}_{prc,c} \qquad \forall c \in (Sld \cup Slt) \quad (20.6)
\end{bmatrix}
\end{bmatrix}
\end{bmatrix}
\vee
\begin{bmatrix}
\neg Y_{prc} \\[4pt]
f_{j,c} = 0 \quad \forall c, j \in (PIN \cup POUT) \quad (20.7)
\end{bmatrix}
\end{bmatrix}
$$

$$\forall prc \in Prt \ (21)$$

When the prc treatment process is selected by means of the activation of the variable Y_{prc}, the Eq. (21.1)-(21.6) are also activated, otherwise Eq. (21.7) is triggered. Eq. (21.1) calculates the initial amount of each component in the reactor in function of the processing time selected (pt_p) and the flow of the compound c in the stream j. Eq. (21.2) and (21.3) determine the medium flow of component c in the output streams of solids and hydrolyzed, respectively, as a function of the final amount of the component in the reactor. *ProdPrcOut* and *HydrPrcOut* are the set of output stream of humid solids and hydrolyzed from each process. Eq. (21.4), (21.5) and (21.6) expresses the kinetic of the solids and solutes approximated by the Crank-Nicholson method. While (21.4) set up the initial point of this method, Eq. (21.6) makes equal the final amount of the compound in the reactor to the value obtained in the last step of the Crank-Nicholson approach. Eq. (21.5) states the calculus of each integration step i of the differential equation system. *Sld* and *Slt* are subsets of the solids and solutes compounds, respectively; *K* is the matrix of coefficients of the differential equations system. The reason to select the integration method is because it is executed in one step, of second order and unconditionally stable (Zienkiewics and Taylor, 2000). Eq. (21.7) must be complied when no process is selected and then input and output stream flows are zero.

In a similar way than Disjunction (21) it is posed disjunction (22) to model the posthydrolysis step. In the case that the dilute acid process is selected the Boolean variable Y_{DAP} is activated and the Eq. (22.1) - (22.7) must be active, otherwise no process is chosen and Eq. (22.8) and (22.9) must be set.

$$
\begin{bmatrix}
Y_{DAP} \\[2mm]
\begin{bmatrix}
f_{19,c} + f_{20,c} = 0 \quad \forall c \in C \quad (21.1) \\
f_{17,c} = f_{18,c} \quad \forall c \in Slv \quad (21.2) \\[2mm]
\bigvee_{p \in P}
\begin{bmatrix}
U_{DAP,p} \\[2mm]
m^{t0}{}_{DAP,c} = tp_p \cdot \sum_{j \in PIN} f_{j,c} \quad (21.3) \\
m^{tf}{}_{DAP,c} = tp_p \cdot f_{j,c} \;\; \forall j \in HydrPrcOut; c \in Slt \quad (21.4) \\[2mm]
\bigvee_{(t \in T; a \in A)}
\begin{bmatrix}
W_{DAP,p,t,a} \\[2mm]
m_{1,c} = m^{t0}{}_{DAP,c} \quad \forall c \in Slt \quad (21.5) \\
\dfrac{m_{i+1,c}}{\Delta t_p} - \dfrac{m_{i,c}}{\Delta t_p} - \dfrac{1}{2} \cdot \sum_{c'} K_{DAP,c,c',t,a} \cdot m_{i,c'} \\
\qquad -\dfrac{1}{2} \cdot \sum_{c'} K_{DAP,c,c',t,a} \cdot m_{i+1,c'} = 0 \;\; \forall i, c \in Slt \quad (21.6) \\
m_{nf,c} = m^{tf}{}_{DAP,c} \quad \forall c \in Slt \quad (21.7)
\end{bmatrix}
\end{bmatrix}
\end{bmatrix}
\end{bmatrix}
\vee
\begin{bmatrix}
Y_{NP} \\[2mm]
f_{17,c} + f_{18,c} = 0 \quad \forall c \quad (21.8) \\
f_{19,c} = f_{20,c} \quad \forall c \quad (21.9)
\end{bmatrix}
\tag{22}
$$

Finally the logic constraint in Eq. (23) completes the model.

$$
Y_{SE} \vee Y_{AH} \vee Y_{DA} \tag{23}
$$

In order to solve the Disjunctive model it was transformed into a Mixed Integer Linear Program (MILP) by means of Big-M type relaxations. The model was implemented in General Algebraic Modeling System (GAMS) (Brooke et al., 1992) and is solved with CPLEX.

5. **Results and discussion**

Based on the developed model it was analyzed the relationship between the maximum of xylose that can be obtained and the amount of cellulose in the solid phase. To perform this analysis, different scenarios are studied by changing the minimum percentage of cellulose in the solid phase, by fixing the corresponding ε parameter. For each scenario, the model returns the amount of xylose recovered as well as the operating variables such as temperature, catalyzer concentration and residence time.

The pairs of values obtained for xylose and cellulose are presented in a Pareto curve that is shown in Fig. 3. The range of cellulose recovery is normally between 96% and 99.5% corresponding to an ε value between 0.96 and 0.995. For lower values of ε, the model returns the same solution. The explanation of this behavior is that a more severe pretreatment is needed to obtain a lower cellulose recovery, this severity gives a greater xylose degradation, this is shown in Fig. 3 in dashed line. Since the model seeks the maximization of this component, as a consequence does not consider such alternatives. In

order to obtain the pair values xylose-cellulose for harsher treatments, the decomposition of cellulose is forced by substituting Eq. (7) by Eq. (24), and varying ε to lower values.

$$f_{22,Cellulose} \leq \varepsilon \cdot f_{1,Cellulose} \qquad (24)$$

Table 1 complements the Fig. 3; it includes information about the pretreatment processes selected (variable Yprc equal to 1) and its operational conditions; it also shows if posthydrolysis stage is active or not, and its operating conditions. In Table 4 can be also observed that the amount of xylose in the hydrolyzed stream diminishes while the amount of cellulose increases above of 96% in the solid output stream. As shown in the table, the model selects the dilute acid pretreatments that have processing time of about 5 minutes, for recoveries greater than 99.5% of the initial cellulose. For lower values of cellulose recovery the Autohydrolysis process is chosen. The Steam Explosion pretreatment process is selected in cases where the cellulose recovery is around 96%; with this process the maximum xylose recovery is obtained. The processing time for the Autohydrolysis and the Steam Explosion pretreatment is between 5 to 30 minutes. The explanation for this behavior is because the model seeks solubilize the hemicelluloses, leaving for the posthydrolysis stage obtaining the monomeric xylose.

From Table 1 can be observed that in all cases it is used a two step process: pretreatment followed by a posthydrolysis. Another conclusion is that a high yield of xylose is obtained with the Steam Explosion pretreatment, although the performance of the Autohydrolysis pretreatment is barely lower. In contrast, for a high recovery of cellulose the Dilute Acid process is selected but the xylose content is lower.
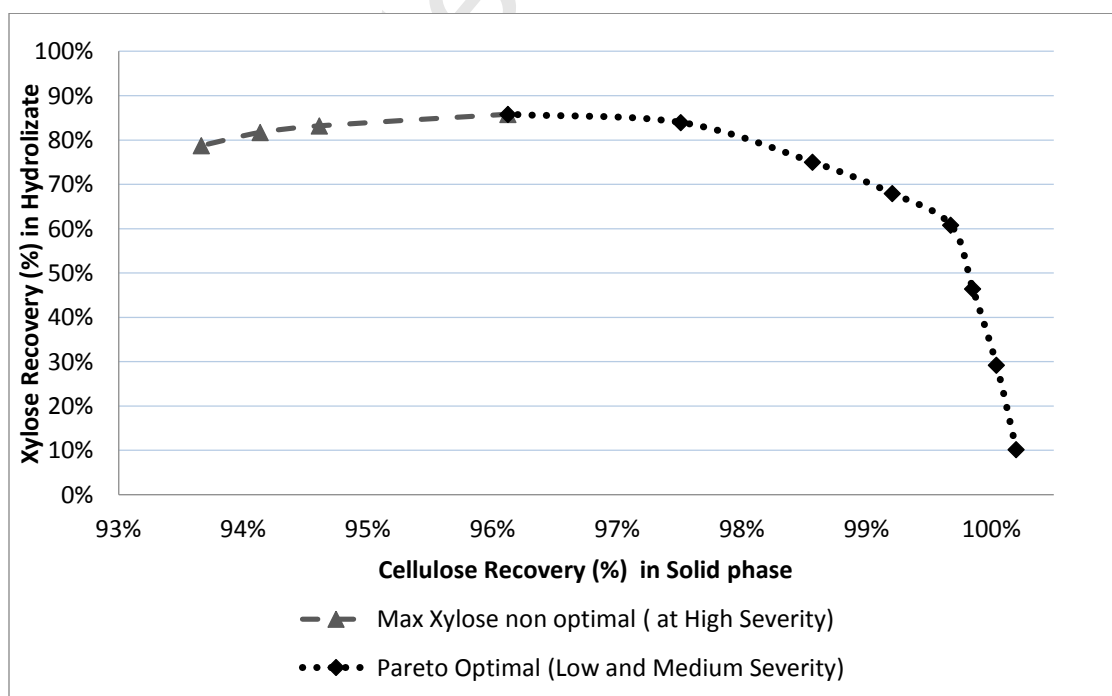

Fig. 3: Maximum Recovery of Xylose and Cellulose.

Pretreatment											
Pretreatment type	DA	DA	AH	AH	AH	AH	AH	SE	AH	AH	AH
Temperature [C]	130	140	200	210	200	200	190	180	190	190	190
Time [min]	5	5	5	5	10	15	30	30	60	65	70
Acid concentration [%]	0,7	1	-	-	-	-	-	-	-	-	-
Posthydrolysis											
Posthydrolysis type	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
Temperature [C]	140	140	140	140	140	140	140	140	130	130	120
Time [min]	8	5	5	5	5	8	5	5	35	40	25
Acid concentration [%]	0,7	0,7	1	1	1	0,7	1	1	0,5	0,5	1
Results											
Xylose Recovery [%] *	10,2%	29,2%	46,4%	60,8%	67,9%	75,0%	83,9%	85,8%	83,2%	81,7%	78,7%
Cellulose Recovery [%] **	99,7%	99,5%	99,4%	99,2%	98,7%	98,1%	97,0%	95,6%	94,1%	93,6%	93,2%
Hemicellulose Recovery [%] **	88,7%	70,2%	52,5%	30,0%	28,6%	15,8%	16,0%	13,2%	4,1%	3,4%	2,8%
Lignin Recovery [%] **	99,5%	98,3%	97,8%	97,7%	95,7%	93,7%	88,5%	73,1%	78,4%	76,9%	75,3%

* Liquid phase; ** Solid phase; DA = Diluted Acid; AH = Autohydrolysis; SE = Steam Explosion.

Table 1: Recovery for various optimal configurations.

As previously mentioned, in all the results obtained the model choses the posthydrolysis stage. Given this result, we decided to analyze the behavior when an only one step process is used (without posthydolysis). For this purpose, the variable Y_{NP} is set to one and the model is executed again. The results can be observed in Fig. 4. The upper curve corresponds to the previous solution, while the lower is related to the case where the posthydrolysis is eliminated. In all cases, the process in one step obtains a lower yield in xylose, but the difference is low, except for those cases where the cellulose recovery is close to 99%. In all cases the selected pretreatment is the Dilute Acid. This is the expected result because the Steam Explosion and the Autohydrolysis treatments are characterized to selectively dissolve the hemicellulose leaving a great proportion of oligo-polysaccharides, giving a lower yield in xylose.

A next step is to evaluate the importance of the influence of performing or not a posthydrolysis stage, concerning the amount of the whole set of fermentable sugars. To perform this analysis, we compare the total amount of fermentable sugars for different enzymatic conversion values. With the supposition that both streams are fermented in different paths, then the main sugars to be treated are: glucose from the enzymatic hydrolysis of cellulose, and xylose dissolved in the hydrolyzed stream. Fig. 5 presents the estimation of the total sugars (Glucose and Xylose) in the results, using yields of enzymatic conversion processes of *E. globulus* reported in the bibliography (Nunes and Pourquie 1996; Romaní, Garrote, and Parajó 2012; Romaní et al. 2010b, 2013, 2014)(Nunes and Pourquie, 1996; Romaní et al., 2010; Romaní et al., 2012; Romaní et al., 2013; Romaní et al., 2014).
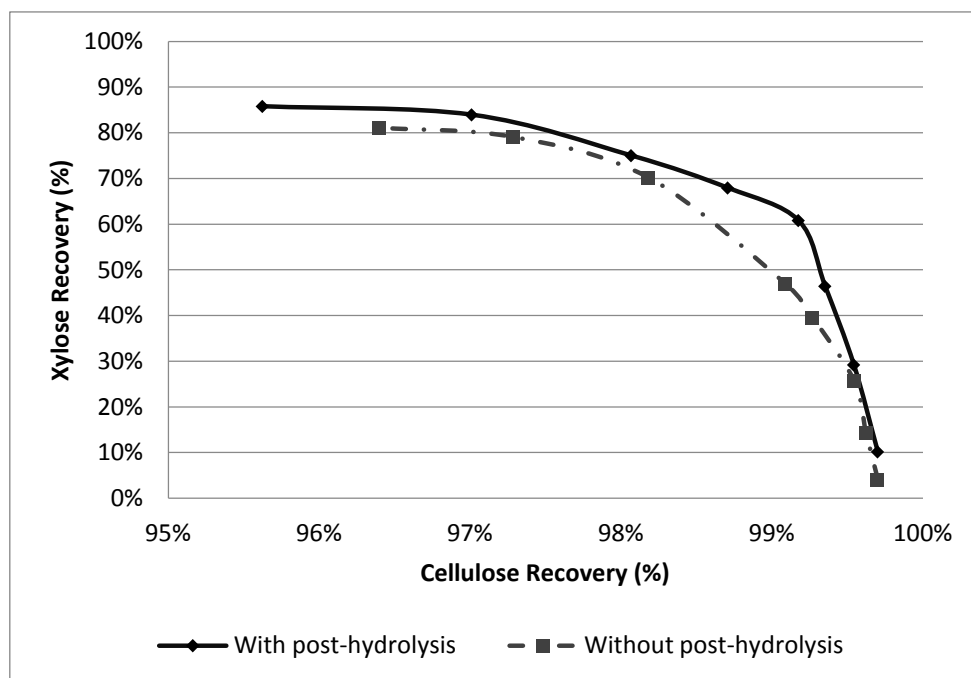
Fig. 4: Xylose recovery with and without posthydrolysis.

Fig. 5 shows that the difference in fermentable sugars between the configuration with and without posthydrolysis is lower than comparing with different values of enzymatic conversion. In other words, the improvement obtained as a result of the posthydrolysis stage is not enough to compensate the decrease in sugars caused by a lower yield in the enzymatic conversion.
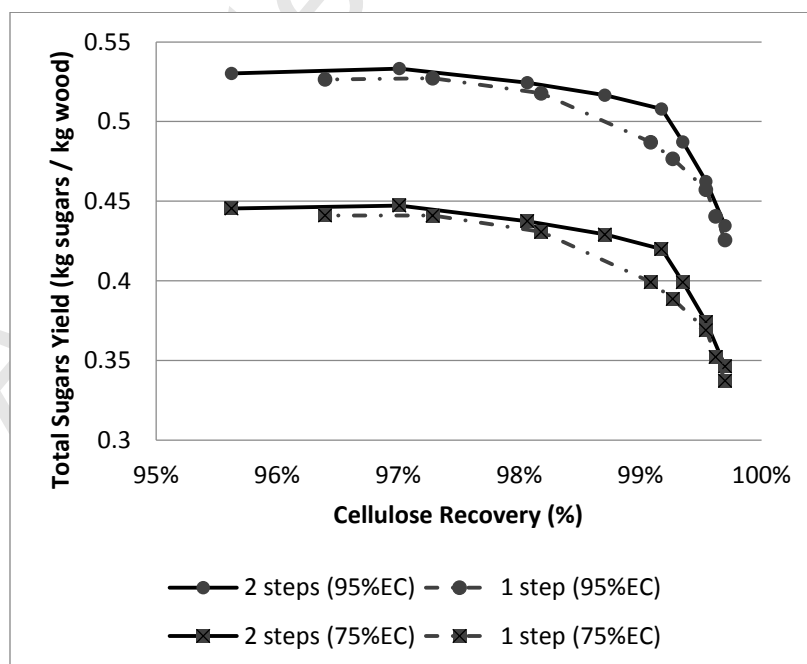

Fig. 5: Total sugars yield for optimal treatments with and without posthydrolysis, and enzymatic conversion yields low and high.

Table 2 contains the yields of total sugars for three enzymatic conversion values, with and without posthydrolysis, where can be corroborated the conclusion obtained .

Total Sugar Yield [kg sugars / kg wood]				
		Enzymatic Conversion		
		75%	85%	95%
Posthydrolysis	YES	0.447	0.49	0.533
	NO	0.441	0.484	0.527

Table 2: Maximum total sugars yield in process with and without posthydrolysis, and for enzymatic conversion yields low and high.
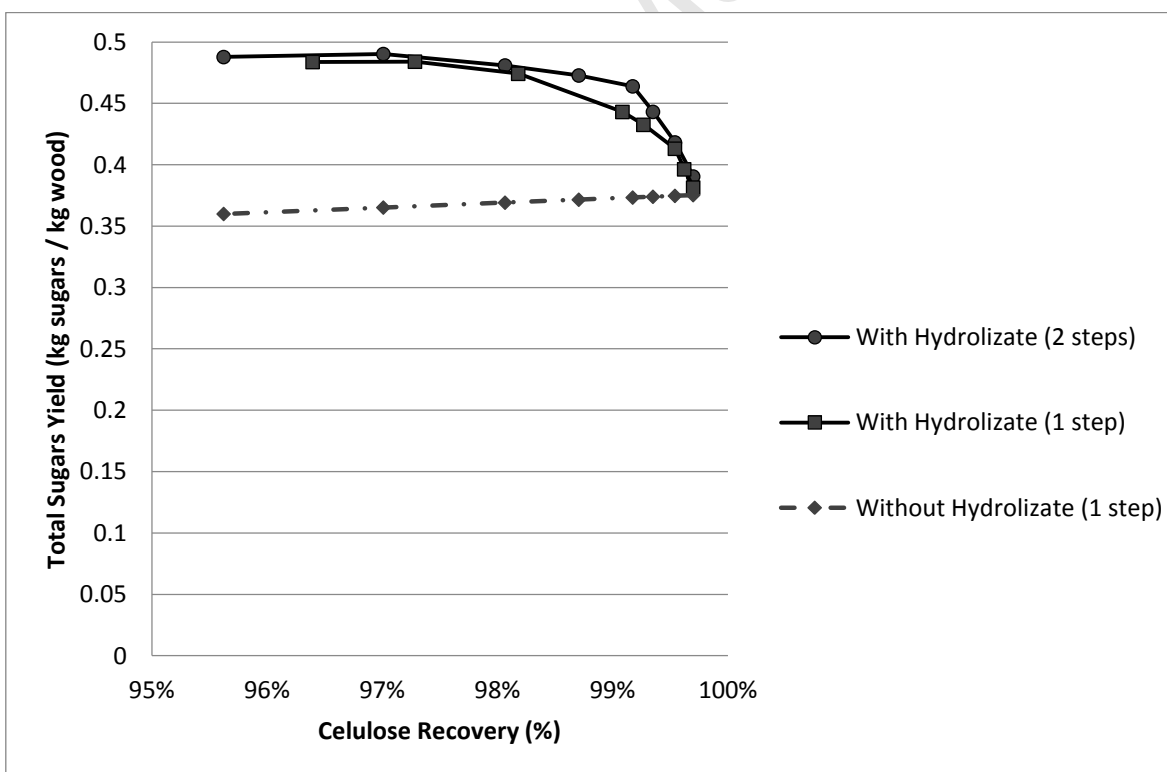

Fig. 6: Total sugars yield, with and without use of hydrolyzed stream, assuming a medium enzymatic conversion of 85%.

Another comparison made is the amount of sugar that can be obtained with the extraction of xylose in the hydrolyzed stream and without it. The results are presented in Fig. 6,

where can be observed that the amount of xylose in that stream can increase in about 30% (best case) the amount of polysaccharides in the hydrolyzed stream. It also confirms that fact that the increase in yield due to the posthydrolysis is very low.

6. Conclusions

This paper deals with different pretreatment processes for ethanol production using *E. globulus* as a raw material, which is a hardwood, with the aim of achieving processing configurations that improve the use of wood polysaccharides. A superstructure presenting the process alternatives is posed. In order to carry out the process synthesis, a two-objective disjunctive program model is proposed, maximizing the recovery of xylose in the hydrolyzed stream and the amount of retained cellulose in solid phase, for subsequent enzymatic hydrolysis. The approach starts considering some previous studies which propose a posthydrolysis step and operation conditions of medium severity to reach a maximum conversion of sugars *versus* the total treated wood. For severe treatments, the amount of recovered xylose is considerably decreased.

Results obtained are consistent with the previous conclusions. However, a small increase is obtained when compared with the value attained with the use of an optimized dilute acid pretreatment. Also, it can be observed that the improvement in the relationship sugar/wood, gained using the posthydrolysis step, has a lower influence in the amount of total sugars when compared with the process having a high enzymatic conversion of cellulose without the posthydrolysis stage.

On the other hand, the increase in the amount of fermentable sugars when maximizing the extraction of xylose could be about 30% compared to only using glucose coming from the enzymatic hydrolysis. Although the maximum benefit of xylose is obtained by using Steam Explosion or Autohydrolysis processes; plus a posthydrolysis step, the results show that using one treatment step of Dilute Acid under controlled operating conditions, results in a yield that is closer to the maximum.

Results attained in this work can help to select an adequate initial configuration stage for the lignocellulosic ethanol process in the case of *E. globulus* and other similar hardwood species. Future works will include the modeling of enzymatic hydrolysis and fermentation stages in order to evaluate the process alternatives regarding bioethanol production yields.

Acknowledgements

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Model Nomenclature

Index

c	Compounds	
j	Connections	
nd	Nodes	
t	Processing times	
t	Temperatures	
a	Acid concentrations	
i	Integration steps	

Continuous variables

$fobj1$, $fobj2$	Objective functions (streams of cellulose and xylose)	kg/h
$f_{j,c}$	Stream of compound *c* in connection *j*	kg/h
F_j^{Sld}	Stream of solids in connection *j*	kg/h
F_j^{Slt}	Stream of solutes in connection *j*	kg/h
F_j^{Slv}	Stream of solvent in connection *j*	kg/h
F_j^{Total}	Total stream in connection *j*	kg/h
$StLoss$	Loss of steam per kg of dry wood.	$kg_{steam}/kg_{dry\ wood}$

Binary variables

Y_{prc}	Decision variable that takes the unit value when the process *prc* is installed	
$U_{prc,p}$	Decision variable that takes the unit value when the piece of equipment *i* and size *t* is installed	
$W_{prc,p,t,a}$	Decision variable that takes the unit value when the piece of equipment *i*, size *t* is installed in number *n*	

Sets

$Inhib_c$	Fermentation inhibitors
Sld_c	Solid compounds
Slt_c	Soluble compounds
Slv_c	Solvent compounds (water)
$NodIN_{j,nd}$	Input connections *j* to node *nd*
$NodOUT_{j,nd}$	Output connections *j* to node *nd*

$WaPrcIN_{prc,j}$	Input of process water j to process prc	
$ProdPrcIN_{prc,j}$	Input stream of product j to process prc	
$WaWashIN_{prc,j}$	Input of washing water j to process prc	
$ProdPrcOUT_{prc,j}$	Product stream output j of a process prc	
$HydrPrcOUT_{prc,j}$	Hydrolyzate stream output j of a process prc	
Prt_{prc}	Pretreatment process	
$PIN_{prc,j}$	$WaPrcIN_{prc,j} \cup ProdPrcIN_{prc,j} \cup WaWashIN_{prc,j}$	
$POUT_{prc,j}$	$ProdPrcOUT_{prc,j} \cup HydrPrcOUT_{prc,j}$	

Parameters

ε	Epsilon parameter for epsilon-constraint	
$MaxCon_c$	Maximum concentration of inhibitors	
$Productivity$	Amount of raw material per hour	kg/h
$RMComp_c$	Raw material composition	
$WSRPrt_{prc}$	Water to solid ratio for pretreatment prc	
$WSRWash_{prc}$	Water to solid ratio for washing prc	
$HOutWash_{prc}$	Humidity of product output	
$SteamExp$	Steam per kg of dry wood for SE process	
pt_p	Processing time	min
T_t	Processing temperature	$°C$
A_a	Acid concentration in acid diluted process	$\%wt$
$K_{prc,c,c',t,a}$	Formation rate of the compound c from c' at temperature t and concentration a of catalyst (see Annex)	$1/min$
$m_{i,c}$	Amount of compound c in the i step of integration	kg
m_c^{t0}	Amount of compound c at initial time	kg
m_c^{tf}	Amount of compound c at final time	kg
Δt_p	Time step for integration when a pt_p processing time has been chosen	min