# Integrated Renewable Production of Sorbitol and Xylitol from Switchgrass

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**Abstract.**

This work deals with the design of integrated facilities for the production of xylitol and sorbitol from lignocellulosic biomass. Xylitol can be obtained from xylose via fermentation or catalytic hydrogenation. Sorbitol is obtained from glucose, but preferably from fructose, also via fermentation or catalytic hydrogenation. Fructose can be obtained from glucose via isomerization. Thus, a superstructure of alternatives is formulated to process switchgrass, corn stover, miscanthus, and others agricultural and forestry residues. Different pretreatments, such as dilute acid or AFEX for the fractionation of the biomass are evaluated. Next, after hydrolysis, the C5 and C6 sugars are processed separately for which a catalytic stage or a fermentation one are considered. Glucose is to be isomerized before it can be processed. Finally, crystallization in a multistage evaporator system is used for purification. The optimization of the system suggests the use of dilute acid and the catalytic system. A system of 3 crystallizers is selected. For a facility that produces 145 kt/yr of xylitol and 157.6 kt/yr of sorbitol, the investment adds up to 120.74 M€ for a production cost of 0.28 €/kg of products. The inverse engineering of biomass was also performed resulting in a composition of 15% water, 20% cellulose, 40% hemicellulose, 15% lignin and 5% ash. The closest biomass corresponds to *Sargassum* (brown algae), that is capable of producing 230.5 kt/yr of xylitol and 116 kt/yr of sorbitol with investment and production costs of 120.5 M€ and of 0.25 €/kg of products, respectively.

**Keywords**: Biorefinery, process and product design, superstructure optimization

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## 1. Introduction

The chemical industry is undergoing a transformation towards a more sustainable future starting from the use of renewable instead of fossil resources, which constitutes the 7th principle of green chemistry[1]. Biomass has emerged as a rich raw material towards the production of energy and chemicals[2]. While energy and fuels focused the first efforts of biorefineries design, such as first and second generation bioethanol,[3, 4] the valorization of biomass towards platform chemicals and added value products is part of this new strategy. Lignocellulosic biomass is a promising feedstock as it consists of cellulose, hemicelluloses and lignin. Glucose is the building block of cellulose and can be used beyond the production of ethanol for the production of hydroxymethylfurfural [5, 6], i-butene[7]. or Sorbitol[8]. Hemicellulose building block is xylen, precursor of xylose that can be converted into furfural,[6] or xylitol among others. Apart from sweeteners, Xylitol and Sorbitol are considered in the production of dietetic foods to diabetics because the not insulin-dependent metabolic pathway They can be used also in pharmaceutical applications (mainly as a carrier), cosmetics industry (as an emulsion stabilizer), moisturizer, texturizer and softener[9]. As a result, Xylitol and Sorbitol have been listed as one of the top 12 high value-added building block intermediate chemicals that can be produced from renewable biomass resources[10, 11].

The chemical synthesis of sorbitol has been evaluated from glucose via catalytic hydrogenation,[12, 13] or from the fermentation of fructose[14, 15] produced via glucose isomerization.[16, 17] In addition techno-economic studies have been performed to evaluate a biorefinery that uses lignocellulosic residues for the production of sorbinol, without considering the use of the hemicellulose.[18] Separately, the xylitol synthesis yield has been evaluated via xylose fermentation[19] as well as hydrogenation.[20] The technoeconomic analysis comparing both synthetic paths has been presented by Mountraki,[21] while biorefineries based on sugarcane lignocellulosic materials towards the production of xylitol, citric acid and glutamic acids have also been presented[22]. However, lignocellulosic biomass contains the building blocks for the production of both products simultaneously and so far no biorefinery considering the production of both has been analyzed.

In this work a mathematical optimization approach has been applied for the systematic comparison of synthesis routes for the simultaneous production of xylitol and sorbitol from biomass. The study allows optimizing the operating conditions of the different units by including surrogate models for all major transformations based on experimental data. The rest of the work is structured as follows. Section 2 presents de description of the superstructure of the alternatives. Section 3 describes the models developed for each one of the steps and technologies. Section 4 shows the solution procedure. In Section 5 the major results of the work are presented including the process design and the economic evaluation of all the pretreatments and synthetic routes applied to switchgrass and biomass of agricultural and forestry origin. A cost comparison is also included using the biomass of optimal composition. Section 6 summarizes the conclusions of the work.

## 2. Overall Process Description

The superstructure used for process synthesis is shown in Figure 1. Biomass must follow a size reduction step before pretreatment. There is a large number of alternative pre-treatments.[2, 23, 24, 25] The ones more widely used are (1) steam explosion-dilute acid ($H_2SO_4$) pretreatment,[1, 26, 27, 28] and (2) ammonia fiber explosion (AFEX).[24, 29, 30] Sorbitol can be produced from glucose while hemicelluloses are used for the production of xylitol.[7] Thus, once the lignocellulosic structure of biomass is broken the cellulose and hemicelluloses are separated. Between both pretreatments only dilute acid pretreatment allows releasing xylose from hemicellulose. The AFEX pretreated biomass requires further hydrolysis at 50ºC. In this case only the xylan is hydrolysated by using the enzyme xylanase to promote the degradation. Similar considerations have been used in previous works as the showed by Aristizábal and Gomez.[31] Cellulose is to be hydrolyzed at 45-50ºC for 3 days to obtain glucose[27, 32, 33, 34].

Glucose and xylose may follow two different pathways to produce sorbitol and xylitol, fermentation and catalytic synthesis. Xylitol can be produced via fermentation using bacteria *Candida guilliermondii*[35], adjusting the operating conditions at 30ºC and 1 bar of pressure with a residence time from 35 h to over 100 h[21]. Sorbitol fermentative production follows two steps: (1) an isomerization stage from glucose to fructose, which is carried out by *Streptomyces sp*. at 70ºC,[17] and (2) fructose fermentation to sorbitol. Xylitol catalytic production is performed in a three phase stirred tank reactor operating between 100-120 °C and 40-60 bar for 60-241 minutes.[36] The reaction is based on Ru catalyst supported generally over NiO, $TiO_2$, activated carbon or zeotype[37, 38, 39]. Sorbitol production follows a similar route. The reaction is carried out also in a three phase stirred reactor employing Ru modified particles[13, 40, 41]. The operating conditions are between 100-140 °C, 40-60 bar [13] for 60-240 min.

The purification process is performed using two parallel multieffect evaporator trains, one per product. For the final products to crystallize, waster is evaporated saturating the xylitol and sorbitol solutions. Commercial steam is used only in the first effect.

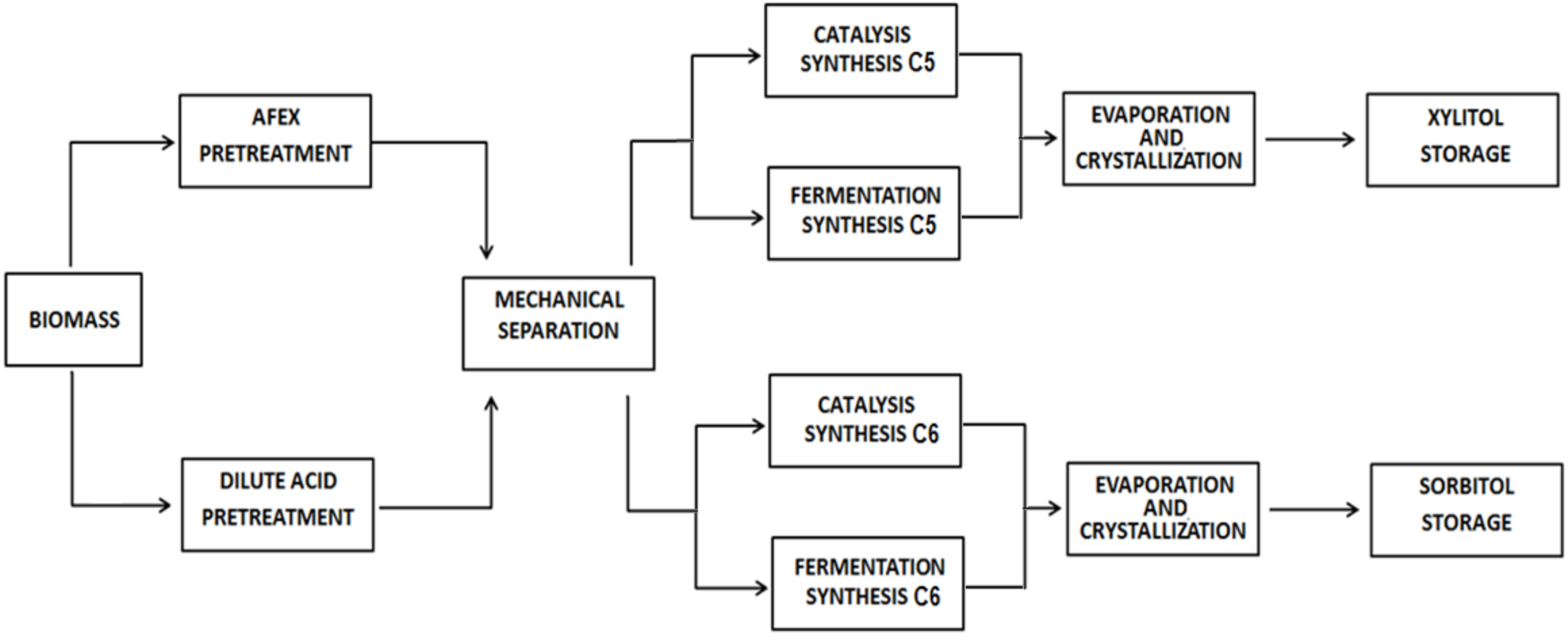

Fig 1. Superstructure for the renewable production of xylitol and sorbitol.

## 3. Mathematical modelling

All the operations in the production of renewable xylitol and sorbitol from switchgrass are modelled with mass and energy balances, experimental yields, thermodynamic and chemical equilibrium and rules of thumb[42]. To model the pretreatments the surrogate models are used taking data from experiments or simulations of the units, ammonia recovery and catalytic xylitol production.

The superstructure is mathematically formulated in terms of temperatures, total and component mass flows and component mass fractions. The components in the system are included in set *J* = { Water, $H_2$, $H_2SO_4$, CaO, Ammonia, Protein, Cellulose, Hemi-Cellulose, Glucose, Xylose, Lignin, Ash, $CO_2$, $O_2$, Cells, Glycerol, Succinic acid, Acetic acid, Lactic acid, gypsum, Ethanol, Xylitol, Sorbitol}.

### 3.1.Pretreatment

The mainl objective of the pretreatment consists of breaking down the raw material. The challenge with lignocellulosic biomass is the complex plant structure. It consists of a matrix of lignin. Within this skeleton, there is a structure formed by for cellulose and hemicellulose, polymers consisting mainly of glucose and xylose linked by o-glycosidic bonds. For the base case, switchgrass is considered as raw material, a native species in the Eastern part of the United States. We can assume a typical composition at the ranges of 15-20 % moisture, 0.25-0.4% Cellulose, 20-30 % Hemicellulose, 15-25 % Lignin and 5.55% Ash. The feedstock is washed and its size is reduced by grinding. This pathway is more effective[2,43]. Both stages, washing and grinding, are considered only in terms of energy consumption (162 $MJ \cdot t^{-1}$)[43] and cost analysis since they do not change the properties of the feedstock. Next, the two alternative pretreatments indicated above, dilute acid pretreatment and AFEX, are analyzed comparing their yield towards structure degradation.[24, 44, 45, 46, 47]

<u>Ammonia fiber explosion (AFEX):</u> This method treats the lignocellulosic biomass with a solution of ammonia at medium-high temperatures and high pressures to break the complex matrix of lignin. To avoid the possible environmental hazards and to reduce the costs of operation, it is necessary to recover the ammonia. The slurry stream rich in water and polymers is sent to an enzymatic process to release the sugars.[24, 29, 30, 48]. Garlock et al (2012)[48] evaluated the yield of this pretreatment for different species of switchgrass. The set of experiments developed studied the effect of the ammonia ratio ($kg \cdot kg^{-1}$ of biomass) and the water load, the operating

temperature (C) and the contact time (min) at 2.1 MPa on the yield of sugars. This operation is carried out in batch mode. To ensure continuous operation, additional reactors in parallel with storage tanks are required.[24, 49] The slurry containing ammonia is sent to a distillation column that operates typically at 3 bar and 140ºC to avoid ammonia decomposition. [26, 50] The pressure may be raised up to 5 bar as long as the amount of ammonia in the slurry is present in traces. In order to obtain the feed, reboiler and condenser temperatures, as well as the purity and the recovery yield as a function of feed composition in ammonia and the operating pressure, a surrogate model developed in previous world[51] from a rigorous simulation of the column in ChemCAD is used. The recovered ammonia is absorbed in water to pressurize a liquid and recycle it.This point is key towards the economic savings, avoiding the compression of ammonia gas. Only 0.5% of the total ammonia is lost in the slurry and can be used as a nutrient in the fermentations downstream.[49] Ammonia make-up is thus fed to the system continuously.

After that we can consider, based on experimental results, that glucose monomer is available in the broth. It will not be the molecule of glucose until the hydrolysis in which the monomer is hydrated, but for the sake of reducing the number of components, a dehydrated glucose is obtained that will be hydrated later on. Xylose is produced from the pretreated biomass via specific hydrolysis in BR1 shown in Figure 2.[51] The complete model and the operational conditions are summarized in *Supplementary Material, AFEX pretreatment.*

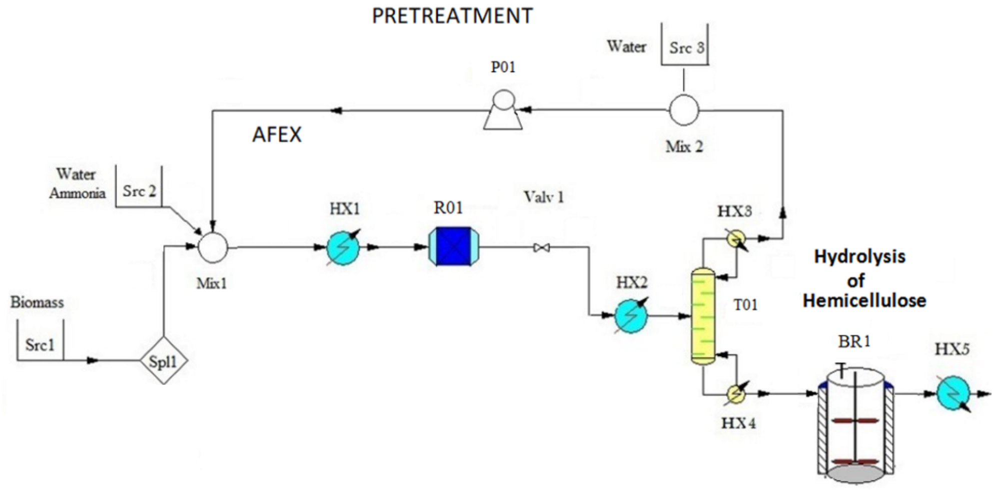

Fig 2. Scheme of the AFEX Pretreatment

Dilute acid**:** This pretreatment uses sulfuric acid and steam explosion to degrade the lignocellulosic structure of biomass. Experimental data on the performance of this pretreatment have been presented in the form of surface response models[52, 53, 54] and mechanistic kinetics.[55] The first approach is more convenient for process synthesis. The yield towards sugars release from biomass depends on the operating temperature, the concentration of the acid, the residence time and the enzyme amount used, per gram of glucan, in the hydrolysis stage.[54] We consider that, as in the previous case, the glucose monomer is generated at this stage but it will be hydrated in the hydrolysis stage to obtain the sugar molecule. The xylose is obtained directly to be used in catalytic or fermentation process. Using the experimental data provided in Shi's paper,[54] surface of response surrogates are developed to estimate the yield of the glucose and xylose released[55].

Next a flash (Flash 1) reduces the water content of the slurry, reducing water consumption and providing energy to the process. The mechanical separation (MecSep 2) allows separating the slurry. The solid phase is bypassed and the liquid phase is neutralized in Reactor 3 using solid lime, CaO.[1, 27, 56, 57] The lime is a cheap chemical the formed gypsum that is easy to separate from the liquid medium[58] using a filtration stage (Filter 1). The optimal time for this reaction is in the range of 3 to 10 minutes. The neutralized liquid stream is mixed adiabatically in Tank 4 with the biomass, and the resulting slurry is sent to hydrolysis. The cellulose needs a further step before it can be broken down into glucose but the xylose is ready to be used eq (1).

$$(C_5H_8O_4)_m + mH_2O \longrightarrow mC_5H_{10}O_5 \qquad \Delta H = 79.0m \ \ \mathrm{kJ \cdot mol^{-1}} \tag{1}$$

The complete model and the operating conditions are summarized in *Supplementary Material, Dilute acid pretreatment.*

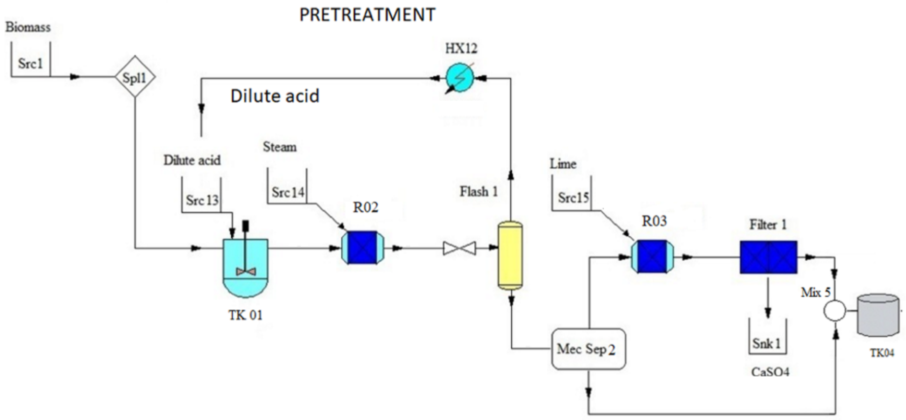

Fig 3. Scheme of the DILUTE ACID Pretreatment

### 3.2. Xylitol and Sorbitol Production by fermentation pathway

The streams rich in xylose and glucose are mechanically separated in a centrifuge separation Mec Sep-1 and Mec Sep-3 depending of the pretreatment. After that process, two parallel streams are obtained, each of them with a different proportion of sugars.

The production of xylitol from xylose fermentation is carried out in fermenter BR-2 by bacterias, immobilized enzyme systems, or fungis as *Candida guilliermondii*[35] adjusting the operating conditions at 30ºC and 1 bar, with a residence time from 35 h to 100 h.[21] Heat exchanger HX-6 and pumps are used to control the temperature and pressure of this operation. The fermentation reaction is as follows:

$$100C_5H_{10}O_5 + 8.75O_2 + 7NH_3 + 37H_2 \longrightarrow 35CH_{1.8}O_{0.5}N_{0.2} + 35CO_2 + 86C_5H_{12}O_5 \qquad \Delta H = -4158.1\ \text{kJ}\cdot\text{mol}^{-1} \qquad (2)$$

During the process, other secondary reactions also take place where Eq (2) is the most important which consumes almost all the xylose, reaching a conversion of 92%.[21]The unconverted xylose remains in the liquid phase. The hydrogen and oxygen needed are directly fed to the fermenter (Src-10 and Src-11 respectively). Ammonia as nitrogen source will also be provided (from Src-4) in the form of an aqueous solution to avoid the temperature increase due to large heat of mixing in BR-2, and to control de input xylose concentration to be in the range of 50-100 g per liter[21]. In this case, the optimal concentration is 100 g per liter because it allows to use the least amount of dilution water possible.

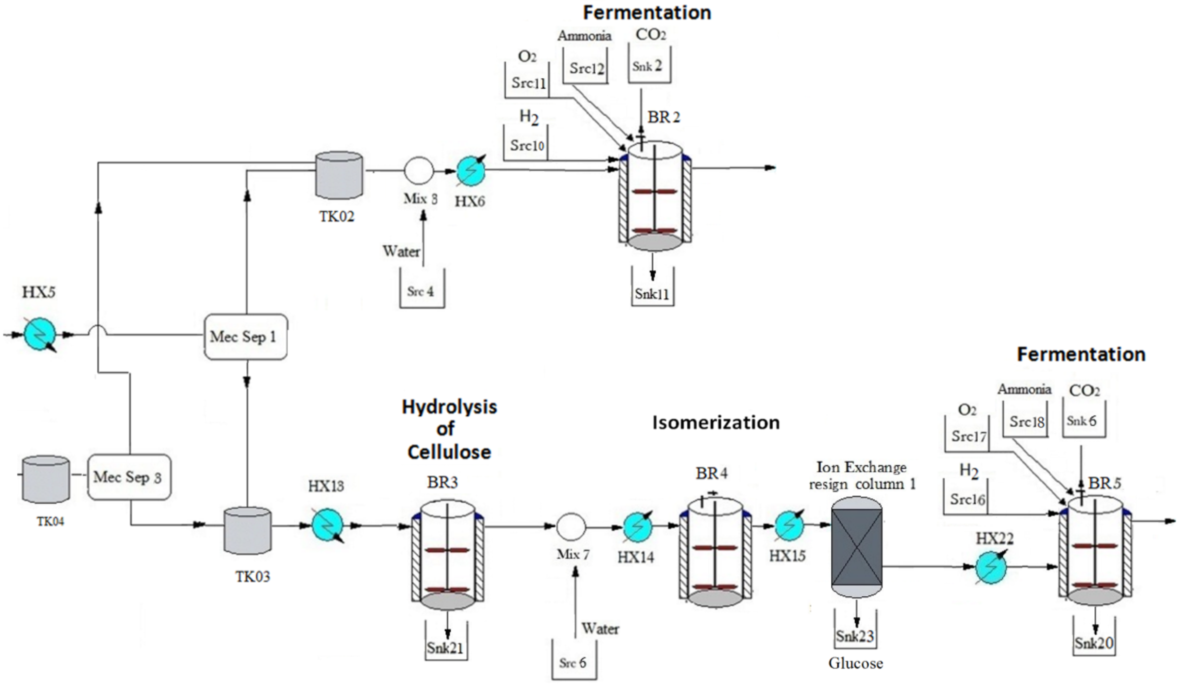

Fig 4. Detail of the Fermentation pathway

The production of sorbitol is carried out by fructose fermentation. The pretreatment releases glucose in the form of a dehydrated molecule. The hydrolysis step takes place to obtain glucose. The next operation consists in the isomerization to fructose,[17] which will be used by *Zymomonas mobilis* in its metabolic route to produce sorbitol.[14] The optimization process of this step consists in optimizing the yield of glucose to fructose, using the rest of glucose as a nutrient for the microorganism and avoiding the secondary reactions. Glucose isomerization is described by eqs (3), (4) and (5).[17]

$$C_6H_{12}O_6\,(\text{glucose}) \longrightarrow C_6H_{12}O_6\,(\text{fructose}) \qquad \Delta\text{H}= 9196 \ \text{kJ}\cdot\text{mol}^{-1} \tag{3}$$

$$K_{isomerization} = \frac{[\text{Fructose}]}{[\text{Glucose}]} \tag{4}$$

$$X_{isomerization} = \frac{[\text{Fructose}]}{[\text{Glucose}]+[\text{fructose}]} x100 \tag{5}$$

The key factors in the isomerization are the temperature and the equilibrium isomerization constant, both related and shown in Table 1.[17]

Table 1.- Range of operating variables for glucose isomerization

| T (°C) | *Kisomerization* | ΔH (kJ/mol) |
|---|---|---|
| 25 | 0.74 | 9196 |
| 40 | 0.92 | 9196 |
| 60 | 1.15 | 9196 |
| 70 | 1.3 | 9196 |

The increase in temperature has a direct effect on the increase in the equilibrium constant of isomerization. Therefore, higher operating temperatures imply higher glucose conversion (see Fig 5), but Takasaki[17] stipulates temperatures of 70 ºC as an upper bound because is the maximum temperature allowed for bacteria *Streptomyces sp*. Values above this limit give rise to the appearance of secondary reactions and a decrease in the enzyme or bacteria activity .

The stream resulting from the isomerization process is conducted to an ion exchange resins column (IER1), where a selective separation of sugars takes place. A stream rich in fructose (> 95%) is obtained. [19] The glucose retained in the column resins can be recovered and then sold as high purity glucose becoming a source of additional process revenue. The stream enriched in fructose is led to a fermentation process (BR-5) where the sorbitol production reaction is carried out, showed in eq (6).

$$100C_6H_{12}O_6 + 15.75O_2 + 7NH_3 + 40H_2 \longrightarrow 35CH_{1.8}O_{0.5}N_{0.2} + 49CO_2 + 86C_6H_{14}O_6 \qquad \Delta\mathrm{H}= -2759.47\ \mathrm{kJ{\cdot}mol^{-1}} \tag{6}$$

As in the xylose fermentation, it is also necessary to adjust the concentration of fructose in the fermentation medium to maximize its conversion. Chung et al. (1988)[14] have studied the conversion of fructose to sorbitol achieved by *Zymomonas mobilis* as a function of some values of fructose concentration. Using those data, a correlation between fructose conversion and its concentration has been developed, eq (7). The graphical representation can be seen in *Supplementary Material, Xylitol and Sorbitol Production by fermentation pathway,* Figure 6.

$$X_{(\mathrm{fructose})} = -1.40{\cdot}10^{-6}(\mathrm{concentration}(\mathrm{g{\cdot}L^{-1}}))^2 + 8.700000{\cdot}10^{-4}(\mathrm{concentration}(\mathrm{g{\cdot}L^{-1}})) + 0.819 \tag{7}$$

The feasible range for the concentration of fructose is between 100 and 300 g/liter, values used to obtain a conversion above 90%. These conditions are necessary to determine the operating conditions in BR-5, since the fructose concentration determines the operation and size of the units downstream.

### 3.3. Xylitol and Sorbitol Production by Catalytic pathway

The streams rich in sugars can also follow a catalytic hydrogenation process in order to obtain xylitol and sorbitol. On the one hand, the stream rich in xylose is directed to the solid-liquid separator S-L separator. In this unit, the lignin is removed, which is considered to be slightly wet, and whose purpose is to obtain pellets to be used as a source of energy for the process. We assume that the remaining hemicellulose is removed here with the lignin. The resulting stream must be heated up to 100-120 °C in HX-07, compressed up to 40-60 bar so that the catalytic hydrogenation reaction eq (8) can be carried out in the reactor (CR-1) for 60-241 min:[36]

$$C_5H_{10}O_5 + H_2 \longrightarrow C_5H_{12}O_5 \qquad \Delta\mathrm{H}= -64.1\ \mathrm{kJ{\cdot}mol^{-1}} \tag{8}$$

The classical method to obtain xylitol from xylose is carried out in a three phase stirred reactor employing as catalyst Ni-Raney[59] or supported Ru modified particles.[36] Ni-Raney presents a lower price and a high catalytic activity.[60, 61] But the disadvantages of this type of catalyst are the leaching of nickel, fast deactivation and nickel dissolution.[13, 37, 60] Thus, catalysts based on supported Ru present a slower desacttivation rate and high selectivity. The supports are generally NiO, $TiO_2$, activated carbon or zeotype[37, 38, 39].

The fresh hydrogen stream is fed to the reactor (CR-1) from the source (Src 5) at the same temperature and pressure as the xylose stream. In the case of introducing an excess of hydrogen to ensure complete conversion of xylose, the membrane MS-1 will be used. The excess of hydrogen is recovered and recirculated to the Mix-9 mixer.

To predict the yield of the reactor, experimental results from the literature[36] have been used to develop a model for the conversion as a function of the reaction time. While, the shape of the profile is sigmoidal and an equation like eq. (9) could be used

$$X_{xylose} = \frac{d}{(1+\mathrm{e}^{(\mathrm{e}+f\cdot \mathrm{RectionTime})})} + g \tag{9}$$

The best fitting was developed using Agustinson equation, eq (10):

$$\frac{\mathrm{ReactionTime}}{X_{xylose}} = \frac{e}{d} + \frac{\mathrm{Re}\,actionTime}{d} \tag{10}$$

This linearization model shows good fitting above 50% conversions, which also leads to better returns. However, the operating conditions depend on the pressure and the temperature. A two stage fitting procedure is used to include the effect of pressure and temperature on the fitting parameters d and e. Table 2 summarizes the parameters d and e belonging to the fittings of Figure 6.

Table 2.- Fitting parameters d and e.

| P (bar) | T (ºC) | d | e |
|---|---|---|---|
| 40 | 100 | 1.4154 | 87.2875 |
|  | 110 | 1.0572 | 11.8766 |
|  | 120 | 1.0045 | 2.5342 |
| 50 | 100 | 1.3168 | 66.3309 |
|  | 110 | 1.0179 | 4.0116 |
|  | 120 | 0.9916 | 0.0533 |
| 60 | 100 | 1.1258 | 26.1553 |
|  | 110 | 1.0288 | 6.0803 |
|  | 120 | 0.9869 | 0.8522 |

The objective of the previous fittings is to determinen the effect of the operating conditions on parameters d and e of the linearization model and to create an model that allows predicting the optimal operating conditions for the catalytic hydrogenation of xylose. The fitting of these parameters are obtained based on parabolas, shown through eqs. (11)-(12).

$$d = d_1 \cdot (\mathrm{T})^2 + d_2 \cdot (\mathrm{T}) + d_3 \tag{11}$$

$$e = e_1 \cdot (\mathrm{T})^2 + e_2 \cdot (\mathrm{T}) + e_3 \tag{12}$$

For each pressure the adjustment coefficients, d1 and e1, d2 and e2 , d3 and e3, corresponding to the quadratic, linear and independent terms are obtained, respectively (summarized in Table 3). The fittings of these coefficients are shown in *Supplementary Material, Parameters fitting* ,Figures S7-S12 .The adjustment coefficients d1, d2 and d3 are summarized in Table 3.

Table 3.- Fitting coefficients d1, d2 and d3

| P (bar) | *d1 (bar $^{-2}$)* | d2 *(bar $^{-1}$)* | d3 |
|---|---|---|---|
| 40 | 0.0015268518 | -0.3564497953 | 21.791809307 |
| 50 | 0.0013628024 | -0.3160760678 | 19.2963948214 |
| 60 | 0.0002761889 | -0.0677064946 | 5.1345819739 |

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$$d_1 = -0,0000046128 \cdot (\mathrm{P})^2 + 0,0003987489 \cdot (\mathrm{P}) - 0,0070425916 \tag{13}$$

$$d_2 = 0,0010399792 \cdot (\mathrm{P})^2 - 0,0895607578 \cdot (\mathrm{P}) + 1,5620137517 \tag{14}$$

$$d_3 = -0,0583319918 \cdot (\mathrm{P})^2 + 5,0003378143 \cdot (\mathrm{P}) - 84,8905163696 \tag{15}$$

The adjustment coefficients e1, e2 and e3 are summarized in Table 4.

Table 4.- Fitting coefficients e1, e2 and e3

| P (bar) | *e1 (min·bar $^{-2}$)* | e2 *(min·bar $^{-1}$)* | e3 |
|---|---|---|---|
| 40 | 0.3303424081 | -76.912997503 | 4475.1631974317 |
| 50 | 0.291804531 | -67.5108775881 | 3899.3733247795 |
| 60 | 0.0742351944 | -17.5968962407 | 1043.4929867889 |

$$e_1 = -0.0008951573 \cdot (\mathrm{P})^2 + 0.0767103691 \cdot (\mathrm{P}) - 1.3058206785 \tag{16}$$

$$e_2 = 0.2025593072 \cdot (\mathrm{P})^2 - 17.2901256531 \cdot (\mathrm{P}) + 290.5971371624 \tag{17}$$

$$e_3 = -11.4004523267 \cdot (\mathrm{P})^2 + 968.4617221371 \cdot (\mathrm{P}) - 16,022.5819653434 \tag{18}$$

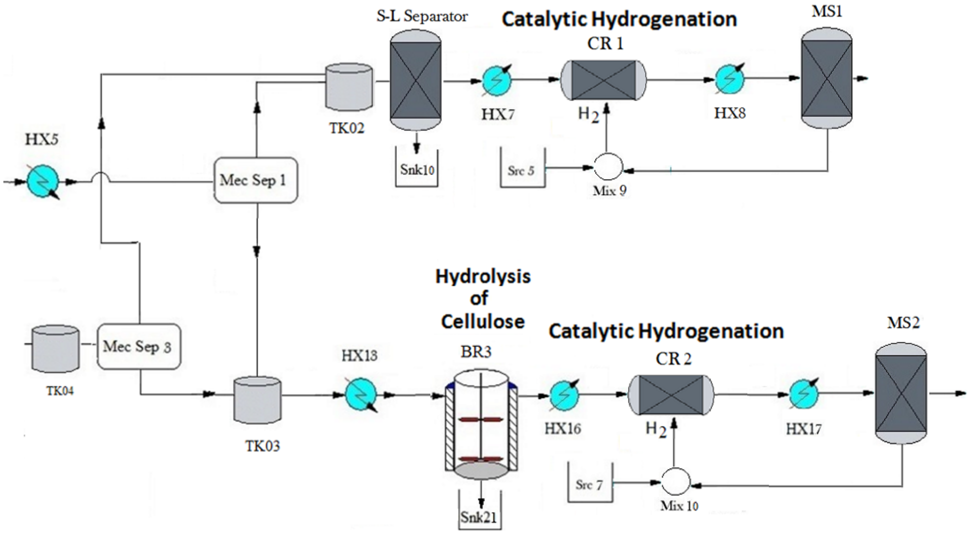

Fig 8. Catalytic pathway

On the other hand, the stream rich in glucose is directed towards heat exchanger HX-16 adjusting the temperature between 100-140 °C, 40-60 bar.[13] before directing it to the catalytic reactor CR-2 .The reaction runs for 60-240 minutes. The synthesis of sorbitol from glucose is carried out in a three phase stirred reactor employing Ru modified particles.[13, 40, 41] Catalysts based on Ni-Raney allows achieving a high conversion of glucose but presents the same disadvantages that the production of xylitol.

$$C_6H_{12}O_6 + H_2 \longrightarrow C_6H_{14}O_6 \qquad \Delta H = -82.7\ \text{kJ}\cdot\text{mol}^{-1} \qquad (19)$$

A fresh stream of $H_2$ at the reaction temperature and pressure is fed from Src-7 to CR-2. It is fed in stoichiometric proportions according to eq (19), but an atmosphere of excess $H_2$ is maintained, which is constantly recovered through the membrane MS-2. As in the case of the production of xylitol production, the excess hydrogen is recovered and recycled to Mix-10. Due to the lack of a time series of the evolution of glucose conversion with respect to temperature and pressure, the modeling of the catalytic reactor and the optimal operating conditions were based on data reported on the conversion of glucose conversion, above of 99.9%. data,[41, 57, 62] and maximizing the amount of sorbitol produced simultaneously minimizing the costs associated with energy (see purification of xylitol and sorbitol).

There are two heat exchangers, HX8- and HX-17 with auxiliary thermal function controlling the temperature of the streams that are directed to the membrane modules in the event that they have a temperature above the allowed one.

### 3.4. Xylitol and Sorbitol Purification

Purification of xylitol and sorbitol is carried out using two sets of multieffect evaporators: Evap1-Evap2-Evap3 and Evap4-Evap5-Evap6 for xylitol and sorbitol respectively. The streams coming from the MS-1 and MS-2 membranes, rich in xylitol and sorbitol, are directed towards HX-11 and HX-20 where their temperatures are adapted depending on the solubility of the different sugars, eqs. (22-25), to improve the purification process.

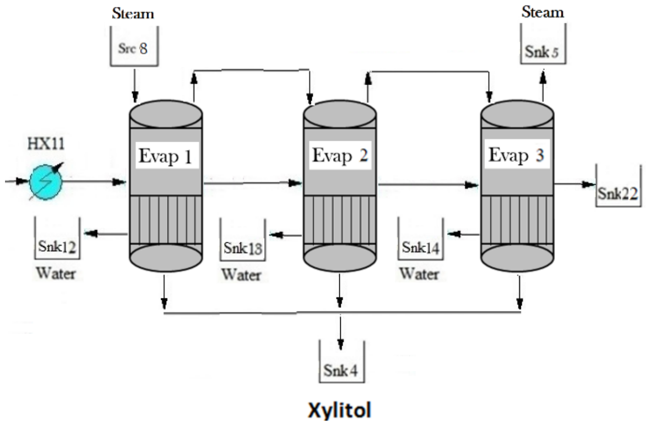

Fig 9 a. Xylitol purification

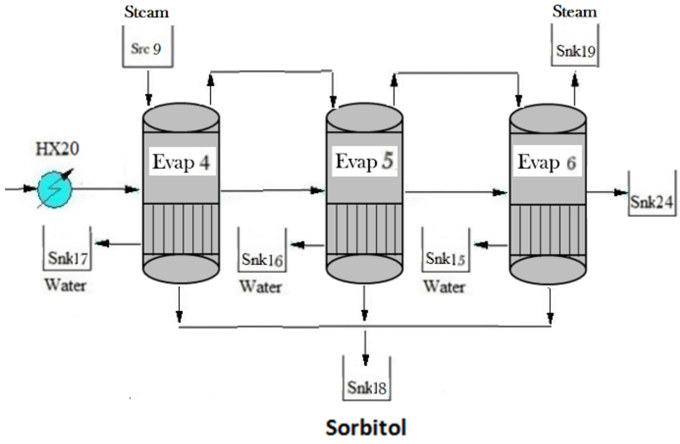

Fig 9 b. Sorbitol purification

The operation of multi-effect evaporators is based on the use of commercial steam in the first one with the aim of evaporating water from the solution and producing a steam that will be used as heating agent in the next effect. The mass balance to the solute is as follows[63]:

$$F_j \cdot \mathrm{x}_{j,f,i} = C_{j,i} + L_j \cdot \mathrm{x}_{j,l,i} \; \forall j \in \{effects\}, i \in \{sugars\} \tag{20}$$

$$x_i = \text{Solubility of species i} \tag{21}$$

Where *x* is given by eqs (20)-(23) for each of the sugar and sugar alcohols:

$$x_{Xylose} = 0.0005 \cdot (\mathrm{T})^2 - 0.003 \cdot (\mathrm{T}) \; - \; 0.9957 \tag{22}$$

$$x_{Xylitol} = 0.2102 \cdot (\mathrm{T})^2 - 6.0031 \cdot (\mathrm{T}) + 201.47 \tag{23}$$

$$x_{Fructose} = 0.0016 \cdot (\mathrm{T})^2 - 0.0196 \cdot (\mathrm{T}) + 3.1655 \tag{24}$$

$$x_{Sorbtol} = 0.1321 \cdot (\mathrm{T})^2 - 0.1578 \cdot (\mathrm{T}) + 166.26 \tag{25}$$

The mass balance to water at the evaporation chamber of each effect is given by eq. (26)

$$f_{water} = Vapor_j + l_{water} \tag{26}$$

This condition is necessary for all sets of evaporators because the steam used in each effect follows an individual way different than the sugars dissolutions. The energy balance for the first effect is given by eq. (27)

$$.\, H_{Sj} + H_{F_d} = H_{sj} + H_{Ej} + H_{Lj} + H_{Crj} \tag{27}$$

while for the following ones the balance becomes as in eq. (28):

$$.\, H_L + H_{Ej} = H_{ej} + H_{Ej+1} + H_{Lj+1} + H_{Crj+1} \tag{28}$$

The enthalpies of the streams are calculated by the components considering enthalpies of formation, crystallization and solution of the solids.

$$H_{F_d} = \sum f_{di} \cdot (\Delta \mathrm{H}_{form\,i} + \int_{T_{ref}}^{T} c_{pi} \cdot dT) \tag{29}$$

where $F_d = \sum f_{di}$ (30)

The rest of liquid streams can be calculated using eqs. (29)-(30).

$\mathrm{H_E}$ is calculated as the enthalpy of a superheated steam since it is generated in a solution whose concentration of sugars increases.

$$H_E = E \cdot (\Delta \mathrm{H}_{form\ Wa(liq)} + \int_{T_{ref}}^{T_{eb}} c_{p,liq} \cdot dT + \lambda(\mathrm{T}_{eb}) + \int_{T_{Teb}}^{T} c_{p,vap} \cdot dT) \tag{31}$$

The rest of vapor streams can be calculated using Eq (31). $\mathrm{H_{cr}}$ is the enthalpy of the crystals and can be calculated with eq (32),

$$H_{Cr} = \sum c_{ri} \cdot (\Delta \mathrm{H}_{form\, i(liq)} + \Delta \mathrm{H}_{cryst\, i} + \int_{T_{ref}}^{T} c_{pi} \cdot dT) \qquad (32)$$

In the optimization process it is very important to take into account that the solutions must go from one effect to the next saturated in the sugar to be recovered. For this, the constraint given by eq. (33) is used:

$$[\mathrm{Sugar}]_i = x_i \qquad (33)$$

Eq. (33) introduces a relevant term in the calculation since the operating conditions change depending on the solubility of the sugar. The model shows different solutions depending of the chemical route. The catalytic synthesis process presents a conversion of xylitol and sorbitol almost of 100%. In this case xylitol and sorbitol are exempted from impurities, allowing easier separations. However, the fermentation shows incomplete conversion of sugars where some amounts of xylose and fructose are swept downstream. Sorbitol is obtained from fructose, but each one has a different solubility, which allows to recover them separately without the risk of having impurities. In the case of xylitol, it should be noted that its solubility is greater than the solubility of xylose, so the presence of certain amounts of xylose in solution results in either the fact that the recovery of xylitol is lower or its purity decreases.

The temperature of the evaporating chamber is calculated using the ebullioscopy increment produced by the presence of the sugars in solution:

$$T = T_{eb} + \sum_i K_b \cdot m_i \qquad (34)$$

$$T = T_{F_d} = T_L = T_C = T_E \qquad (35)$$

where $K_b$ is the boiling constant of water, 0.512 kg / (mol K) and $m_i$ is the molality of each sugar. The pressure of each chamber is provided as function of $T_{eb}$ using the Antoine´s equation

$$P_j = e^{(18.3036 - \frac{3816.44}{T_{eb}+227})} \qquad (36)$$

The additional process constraints are provided by eq (37) and eq (38) .

$$P_j \geq P_{j+1} \qquad (37)$$

$$T_j = T_{j+1} + 10 \qquad (38)$$

## 4. Solution procedure

For simplicity, due to the presence of only one binary variable, the one related to the selection of the pretreatment, two nonlinear optimization models (NLP's) are solved involving 2700 equations and 3800 variables each. The major decision variables are the operating conditions at the pretreatment reactors, feed ratios and temperatures of operation, the operating conditions at the synthesis, the split fraction, operating pressures and temperatures at the evaporators sets. This last one depends on the yield of each pretreatment as well as the biomass composition. The model is solved using a multistart optimization approach in GAMS with CONOPT 3.0 as the preferred solver. The objective function is profit maximization including xylitol and sorbitol production, and the thermal energy and hydrogen consumed due to the fact that it is the largest variable cost, eq. (39):

$$Z = P_{Xylitol} fc_{Xylitol} + P_{Sorbitol} fc_{Sorbitol} - P_{Steam} \sum_i \frac{Q_i}{\lambda} - P_{H_2} fc_{H_2} \tag{39}$$

Next, a heat exchanger network is developed[64] and an economic evaluation is performed to compute production and investment costs. [65] The production cost involves annualized equipment, chemicals (enzymes, sulfuric acid, CaO, ammonia, and the profit from gypsum), labor, utilities, raw material, and the credit that can be obtained from glucose excess. The costs for utilities are updated from the literature, 19 $\$\cdot t^{-1}$ Steam, 0.057 $\$\cdot t^{-1}$ cooling water, Electricity: $1.7\cdot10^{-8}$ $\$\cdot J^{-1}$ [66] and the base price for biomass is 100€/t. The estimation of the investment is performed with the factorial method.[65] First, the equipment cost is estimated with the mass and energy balances obtained from the optimization. The cost for the equipment such as heat exchangers, fermenters, tanks, distillation column, mechanical separation, filters, molecular sieves is updated from the values calculated using the correlations developed by the authors; see supplementary material of Martín & Grossmann (2011)[3] and Almena and Martín (2015)[67]. Next, the equipment cost is calculated as a function of the equipment cost, using factors of 3.15 and 1.4. These factors correspond with a facility processes fluids and solids for the physical and total fixed costs[65].

The economic study is followed by the analysis of the operation of different biomass types towards the production of xylitol and sorbitol.

## 5. Results

The facility is based on a feed of 18 kg/s of biomass is used typical from bioethanol production facilities and biomass processing[68] using switchgrass as base case.

## 5.1.- Facility operation

Tables 5, 6 and 7 summarize the operating conditions of the pretreatments and synthesis paths and the purification of xylitol and sorbitol carried out in the evaporators.

Regarding the pretreatments conditions, the dilute acid requires a higher temperature than AFEX process, 180ºC vs 110ºC, that together with the presence of the acid allows to degrade a higher amount of hemicellulose to xylose. However, note that the acid can dehydrate the sugars into furfural and furans, inhibitors for fermentation. We assume that it is not the case. AFEX pretreatment requires higher pressure to break down the lignocellulosic structure of biomass and an additional stage for the hydrolysis of the hemicellulose that carried out in a fermenter at 50ºC and 1 bar.

Within the synthesis routes, the catalytic process makes use of high pressures, close to 48 bar, and moderate temperatures of 100ºC or higher. Optimizing process energy and increasing xylose and glucose conversion allows operation at or near the lower limit of the operating conditions.[13, 36] The fermentation process operates at mild pressure and temperature conditions, typically at 1 bar in all cases, using 30ºC for the xylose and fructose fermentations, and 70ºC for the isomerization of glucose to fructose. Fermentation results in obtaining lower sugar conversion rates due to the bacteria metabolism of *Candida guilliermondii*[35] and *Zymomonas mobilis*[14], use of larger volumes to feed and increase the treatment time.

Table 5.- Pressure and temperature for the pretreatments.

| | Dilute Acid-Catalysis Hydrogenation | | AFEX-Catalysis Hydrogenation | | Dilute Acid-Fermentation | | AFEX-Fermentation | |
|---|---|---|---|---|---|---|---|---|
| | P (bar) | T(ºC) | P (bar) | T(ºC) | P (bar) | T(ºC) | P (bar) | T(ºC) |
| Reactor 1 | - | - | 21 | 109.8 | - | - | 21 | 109.3 |
| Reactor 2 | 1 | 180 | - | - | 1 | 180 | - | - |
| Reactor 3 | 1 | 107.4 | - | - | 1 | 105.4 | - | - |
| Hydrolysis of Hemicellulose (BR1) | - | - | - | - | 1 | 50 | 1 | 50 |
| Hydrolysis of Cellulose (BR3) | 1 | 50 | 1 | 50 | 1 | 50 | 1 | 50 |

Table 6.- Pressure and temperature for the synthesis.

| | Dilute Acid-Catalysis Hydrogenation | | AFEX-Catalysis Hydrogenation | | Dilute Acid-Fermentation | | AFEX-Fermentation | |
|---|---|---|---|---|---|---|---|---|
| | P (bar) | T(ºC) | P (bar) | T(ºC) | P (bar) | T(ºC) | P (bar) | T(ºC) |
| Catalytic Reactor CR1 | 46.86 | 104.43 | 47.92 | 100 | - | - | - | - |
| Catalytic Reactor CR2 | 46.87 | 100 | 47.9 | 100 | - | - | - | - |
| Fermenter BR2 | - | - | - | - | 1 | 30 | 1 | 30 |
| Fermenter BR4 | - | - | - | - | 1 | 70 | 1 | 70 |
| Fermenter BR5 | - | - | - | - | 1 | 30 | 1 | 30 |

The optimal operating conditions for each of the four alternative processes show the use of vacuum pressures to reduce the amount of commercial steam. Since all the processes work under approximately the same conditions of pressure and temperature, the comparison among the alternatives is performed based on the following ratios $kg_{steam}/kg_{xylitol}$ and $kg_{steam}/kg_{sorbitol}$ (Table 7). Catalytic synthesis processes use a significantly smaller amount of steam in the evaporators, due to the higher concentration of xylitol and sorbitol. These processes show higher conversion of glucose and xylose. However, fermentative synthesis processes require the use of large volumes of cell cultures, which implies lower conversions of sugars and the use of larger amounts of commercial steam. The difference in the operating condition it also due to the pretreatment yield. The dilute acid pretreatment has higher production rates of cellulose and hemicellulose than the AFEX pretreatment. As a result, the yield to xylitol and sorbitol is larger increasing the product concentration in the streams. Thus, the boiling point of the mixture increases, requiring the use of more steam in the evaporators since the operating pressure should not be further reduced. In addition, the fermentative synthesis processes require the proper concentration of xylose,[35] for which it is necessary to dilute it with more water that is later removed in the evaporators.

Table 7.- Pressure and temperature for the evaporators.

| | | Dilute Acid-Catalysis Hydrogenation | | AFEX-Catalysis Hydrogenation | | Dilute Acid-Fermentation | | AFEX-Fermentation | |
|---|---|---|---|---|---|---|---|---|---|
| | | P (mmHg) | T(ºC) | P (mmHg) | T(ºC) | P (mmHg) | T(ºC) | P (mmHg) | T(ºC) |
| Xylitol | Evap1 | 119.31 | 55.24 | 112.92 | 54.10 | 152.99 | 60.53 | 161.04 | 60.53 |
| | Evap2 | 108.88 | 53.35 | 107.27 | 53.04 | 145.34 | 59.42 | 145.34 | 59.42 |
| | Evap3 | 52.67 | 39.15 | 48.92 | 37.78 | - | - | - | - |
| | $kg_{steam}/kg_{xylitol}$ | 0.23 | | 0.20 | | 7.17 | | 7.15 | |
| Sorbitol | Evap4 | 148.7 | 59.91 | 145.11 | 59.39 | 152.79 | 60.50 | 151.81 | 60.36 |
| | Evap5 | 141.26 | 58.81 | 137.86 | 58.29 | 145.15 | 59.39 | 144.22 | 59.26 |
| | Evap6 | 133.06 | 57.54 | 126.07 | 56.40 | 123.26 | 55.92 | 121.56 | 55.63 |
| | $kg_{steam}/kg_{sorbitol}$ | 1.09 | | 0.76 | | 2.76 | | 2.26 | |

Table 8 shows the main operating ratios used to compare the alternative production paths. It can be observed that the yield to xylitol and sorbitol is lower in the fermentation paths, due to the lower conversion of the bacteria cultures. The best processes for obtaining xylitol and sorbitol are designed using the catalytic path. Within the catalytic process, the dilute acid pretreatment allows obtaining a larger concentration of sugars than the AFEX pretreatment, resulting in higher ratios of xylitol and sorbitol per kilogram of biomass and requiring less steam in their purification.

Table 8.- Major yields of the alternative production paths

| | Dilute Acid- Catalysis Hydrogenation | AFEX- Catalysis Hydrogenation | Dilute Acid- Fermentation | AFEX- Fermentation |
|---|---|---|---|---|
| $kg_{H2}/ kg_{Biomass}$ | 0.007 | 0.005 | 0.001 | 0.001 |
| $kg_{H2SO4}/ kg_{Biomass}$ | 0.024 | - | 0.017 | - |
| $kg_{NH3}/ kg_{Biomass}$ | - | 1.052 | - | 1.052 |
| $kg_{Xylitol}/ kg_{Biomass}$ | 0.259 | 0.187 | 0.166 | 0.120 |
| $kg_{Sorbitol}/ kg_{Biomass}$ | 0.282 | 0.231 | 0.142 | 0.102 |
| $kg_{Steam}/ kg_{Biomass}$ | 0.505 | 0.587 | 2.013 | 1.374 |

### 5.2.- Economic evaluation

The economic evaluation is performed to both pretreatments and both synthesis processes, obtaining four alternative production paths, computing the production and investment costs. The detailed investment and production costs for the alternative production paths are shown in Figure 10. Table 9 summarizes the total costs, which increase when the fermentation paths are selected. In general, the fermentation process working in continuous operation needs several fermenters operating in parallel. This, together with the need for larger volumes of flows to be treated and larger needs for steam used (Tables 7 and 8) in the evaporators to concentrate the streams, results in larger costs. Regarding the pretreatments, AFEX involves higher costs than the dilute acid pretreatment referred to catalysis hydrogenation due the need for a distillation column to recover the ammonia employed and an additional stage of hemicellulose hydrolysis, which explains the difference of 57% and 51% in pretreatment costs between AFEX and Dilute Acid Catalytic Hydrogenation (Figures 10 d and h). The fermentation paths feature the opposite behavior. This can be explained because the increase in the amount of sugars implies the use of more water to adjust the xylose concentration at the fermenter, requiring a larger number of fermenters and larger amount of commercial steam. This can be seen comparing the investment costs of heat exchangers (HX), which reach 46% and 58% for AFEX and Dilute Acid respectively (Figures 10 b and f). This can also be observed in the percentage of utilities of production costs, reaching values of 18% and 22% of the total respectively (Figures 10 a and c). From Figures 10 b, d, f and h it can be concluded that Dilute Acid pretreatment is cheaper than AFEX pretreatment.

Based on the major yields (Table 8) and lower investment and production costs (Table 9), the best process to obtain xylitol and sorbitol from switchgrass is the one that uses Dilute Acid as pretreatment and catalytic hydrogenation as a synthetic path.

Table 9.- Investment and production costs of the alternative production paths

| | Dilute Acid-Catalysis Hydrogenation | AFEX-Catalysis Hydrogenation | Dilute Acid-Fermentation | AFEX-Fermentation |
|---|---|---|---|---|
| Investment (M€) | 120.8 | 146.4 | 323.7 | 273.5 |
| Production Cost (M€/yr) | 18.7 | 22.9 | 45.8 | 37.8 |

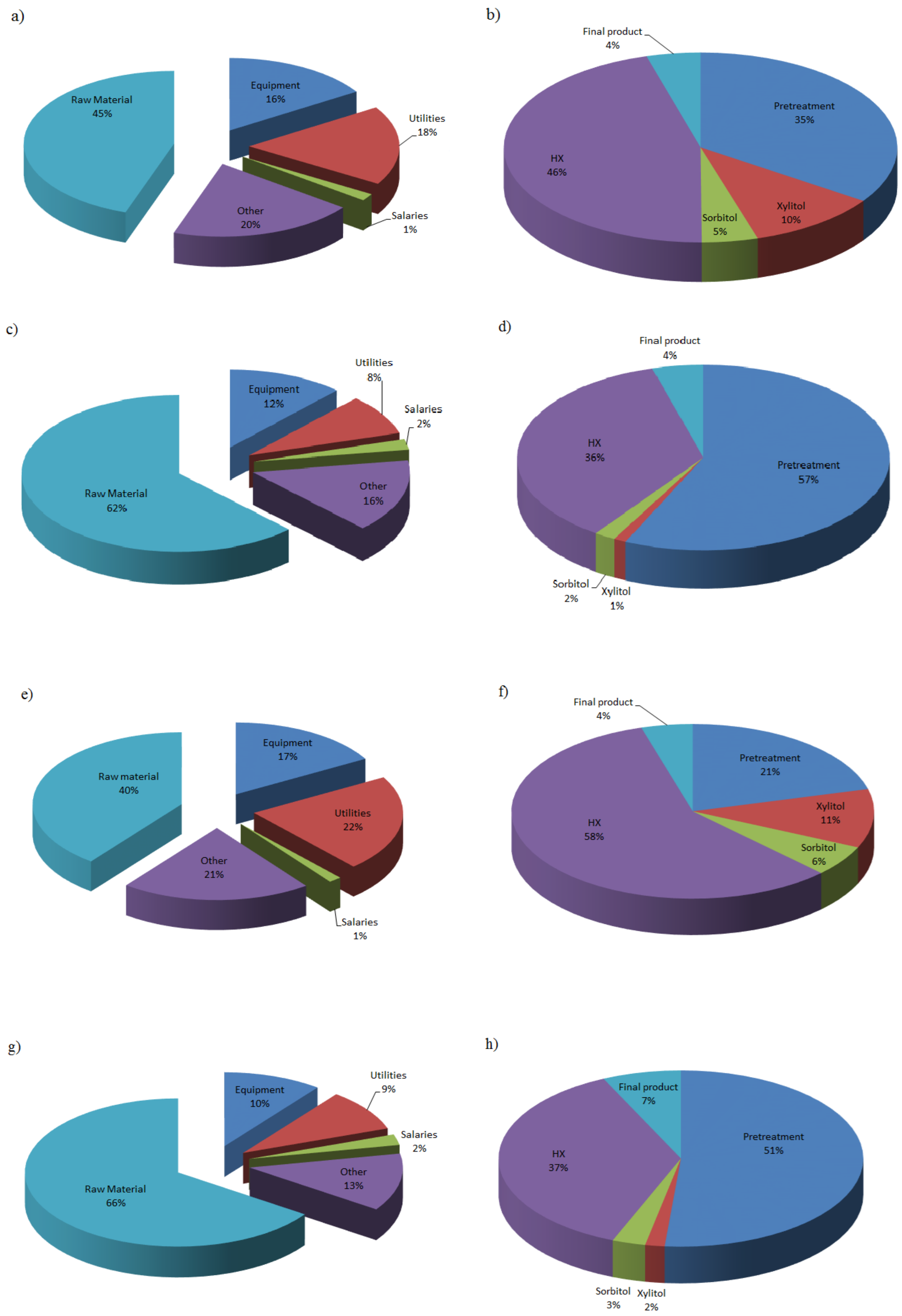

Fig 10. Detailed productions costs and investment costs for AFEX-Fermentation (a and b), AFEX-Catalytic Hydrogenation (c and d), Dilute Acid-Fermentation (e and f) and Dilute Acid- Catalytic Hydrogenation (g and h).

## 5.3.- Biomass design and evaluation

### 5.3.1.-Evaluation of different raw materials

Once the dilute acid and catalytic synthesis are selected as the best pretreatment and synthetic paths, the analysis developed for switchgrass is applied also to evaluate other typical biomasses such as corn stover, forest residues like a birch, pine and spruce, hybrid poplar, sugar bagasse and wheat straw. The results are summarized in Table 10 with each biomass composition. The composition of water has a direct effect in the steam ratio and a larger amount of water the steam is neededy to adjust the xylitol and sorbitol concentration increases. Furthermore, the increase in the percentage of water implies the increase in the amount of sulfuric acid used in the pretreatment. In the same way, the proportions of xylitol and sorbitol increase with a larger composition of hemicellulose and cellulose in the biomass, demanding a larger consumption of hydrogen. In general, the amount the lignin plays a fundamental role in the costs since it is biomass that cannot be transformed into products. In addition, an increase in the lignin content implies a higher energy consumption in the pretreatment and the increase in production and investment cost, in spite of the possible production of energy. This energy is estimated considering a boiler efficiency of 75% and 26,100 kJ per kilogram of lignin as an average value of heat of combustion. To be on the safe side, the credit out of this energy has not been included in the economic analysis, Based on these criteria and analyzing the data from Table 10, the biomass that offers the best results is corn stover, which is widely available in large parts of the world.

Table 10.- Major yields, investment and production costs for the different biomasses (abbreviations: W= water; C=cellulose; HC=hemicellulose; L=lignin; A=ash)

| Biomass | Composition (%) | | | | | Production cost (M€/yr) | Investment cost (M€) | Product cost (€/kg) | kg $_{Xylitol}$/ kg $_{Biomass}$ | kg $_{Sorbitol}$/ kg $_{Biomass}$ | kg $_{H2SO4}$/ kg $_{Biomass}$ | kg $_{H2}$/ kg $_{Biomass}$ | kg $_{Steam}$/ kg $_{Biomass}$ | Energy from lignin (kW) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | W | C | HC | L | A | | | | | | | | | |
| Switchgrass | 18.62 | 31.98 | 25.15 | 18.40 | 5.85 | 18.7 | 120.8 | 0.283 | 0.259 | 0.282 | 0.024 | 0.007 | 0.505 | 67,495 |
| Corn stover | 16.95 | 41.05 | 31.39 | 6.34 | 4.27 | 16.3 | 111.7 | 0.220 | 0.323 | 0.361 | 0.023 | 0.078 | 0.386 | 25,663 |
| Birch (Forest Residue) | 3.80 | 43.90 | 28.90 | 20.20 | 3.20 | 19.2 | 124.8 | 0.225 | 0.297 | 0.386 | 0.021 | 0.009 | 0.350 | 74,228 |
| Pine (Forest Residue) | 5.00 | 40.70 | 26.90 | 27.00 | 4.00 | 20.4 | 129.6 | 0.244 | 0.323 | 0.358 | 0.021 | 0.072 | 0.353 | 97,973 |
| Spruce (Forest Residue) | 2.00 | 42.00 | 27.30 | 27.40 | 1.30 | 20.5 | 130.1 | 0.238 | 0.281 | 0.370 | 0.023 | 0.074 | 0.347 | 99,421 |
| Hybrid poplar | 6.91 | 50.80 | 26.20 | 15.50 | 5.90 | 18.4 | 121.5 | 0.213 | 0.270 | 0.447 | 0.022 | 0.080 | 0.357 | 57,374 |
| Sugar Bagasse | 7.00 | 41.00 | 30.10 | 21.20 | 7.00 | 19.4 | 125.5 | 0.230 | 0.310 | 0.361 | 0.022 | 0.076 | 0.361 | 77,889 |
| Wheat Straw | 8.43 | 40.26 | 30.56 | 16.52 | 4.23 | 18.5 | 121.5 | 0.228 | 0.315 | 0.354 | 0.022 | 0.076 | 0.364 | 61,446 |

### 5.3.2- Biomass design

As complementary objective of this work, instead of using a fixed biomass composition, belonging to a lignocellulosic species such as switchgrass, the optimal flowsheet is used to determine the best composition within the typical ranges of hemicelluloses, cellulose and lignin for the simultaneous production. The resulting composition is compared with a database to determine the most suitable biomass. In this way the resulting biomass composition correspond to 15% water, 20% cellulose, 40% hemicellulose, 15% lignin and 5% ash. One that fits the best is sargassum algae (*sargassaceae*) with a composition of 20.48% cellulose and 43.19% hemicellulose. The production and investment cost for this biomass are 18.4 M€/yr (0.25 €/kg) and 120.5 M€ respectively. The breakdown in the costs are shown in Figure 11. Table 11 compares the major values for switchgrass and sargassum algae with slightly better values for the last of the two.

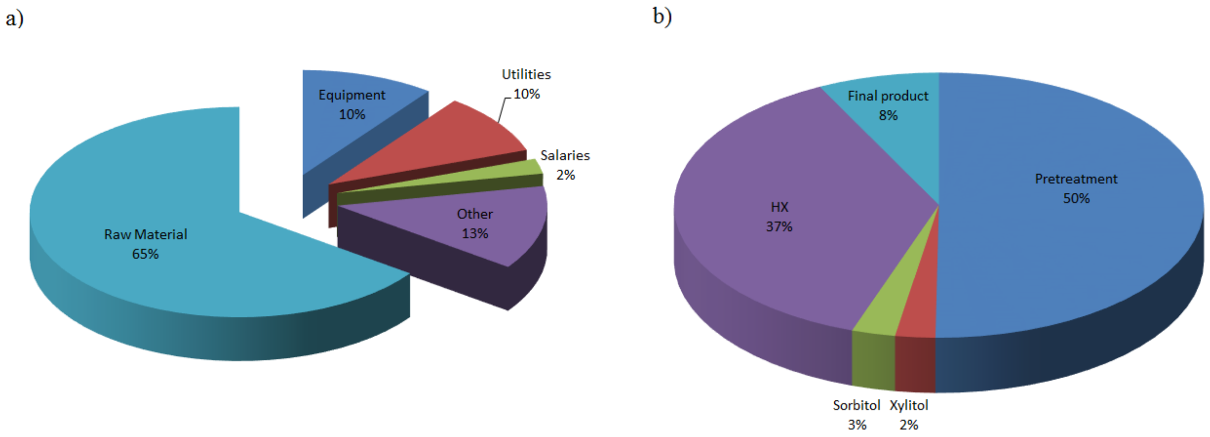

Fig 11. Dilute Acid- Catalytic Hydrogenation Free Composition productions costs (a), investment costs (b)

Table 11.- Investment and production costs comparative between switchgrass and sargassum algae

| | Dilute Acid-Catalysis Hydrogenation switchgrass | Dilute Acid-Catalysis Hydrogenation Sargassum algae |
|---|---|---|
| Investment (M€) | 120.8 | 120.5 |
| Production Cost (M€/yr) | 18.7 | 18.4 |
| Xylitol (kg/$kg_{Biomass}$) | 0.26 | 0.41 |
| Sorbitol (kg/$kg_{Biomass}$) | 0.28 | 0.21 |

To determine if this biomass is more promising than switchgrass, we compare the production and investment costs (Table 11). It can be seen that both biomasses yieldt similar values. The larger difference between them is the ratio of xylitol and sorbitol produced per kg of biomass. While the amount of xylitol and sorbitol produced are of 0.26 and 0.28 kg per kg of biomass for switchgrass, while in the case of the sargassum algae, values of 0.41 and 0.21 are achieved, respectively. The difference in the market prices of xylitol and sorbitol (3900$/ton and 650$/ton)[69] isuggests to choose a larger quantity produced of the product with a higher selling price. Thus, the key parameter is a larger amount of xylitol produced per kg of biomass. The difference also explains the choice of sargassum algae as the best biomass, and not the corn stover (Table 12).

Table 12.- Xylitol and sorbitol production comparative between switchgrass, sargassum algae and corn stover.

| | Dilute Acid-Catalysis Hydrogenation switchgrass | Dilute Acid-Catalysis Hydrogenation Sargassum algae | Dilute Acid-Catalysis Hydrogenation Corn stover |
|---|---|---|---|
| Xylitol production ( kt/yr) | 145 | 230 | 181 |
| Sorbitol production ( kt/yr) | 157.6 | 116 | 202 |
| Xylitol (kg/kg$_{Biomass}$) | 0.26 | 0.41 | 0.32 |
| Sorbitol (kg/kg$_{Biomass}$) | 0.28 | 0.21 | 0.36 |

## 6. Conclusions

Xylitol and sorbitol production from lignocellulosic biomass has been evaluated within the integrated biorefinery concept. Four different chemical paths are considered for the production of xylose and glucose and the final products. The biorefinery is modelled using first principles and surrogate models for each one of the operations. The selected option is dilute acid as the pretreatment and catalytic hydrogenation as synthetic path. Assuming that no inhibitors are produced, for a facility that produces 145 kt/yr of xylitol and 157.6 kt/yr of sorbitol, the investment adds up to 120,8 M€ for a production cost of 0.28€/kg. Integrated facilities operate at their optimum for specific biomass compositions. This framework also allows evaluating the best use of each biomass used depending on its composition, as long as the models for the pretreatments are valid. Within the biomass used, corn stover is chosen as the best option, resulting in a production capacity of 181 kt/yr of xylitol and 202 kt/yr of sorbitol, while the investment adds up to 112 M€ for a production cost of 0.22€/kg.

As a complementary study, the optimal biomass design was performed. Among all of components, hemicellulose and cellulose are selected because they are the sources of sugars. Thus, the optimal biomass is the one that provides the closest composition with an existing biomass. For this case, the optimal composition of those components obtained was 20% cellulose and 40% hemicellulose, finding the closest composition of

20.48% cellulose and 43.19% hemicellulose in sargassum algae (*sargassaceae)* biomass. For this biomass, 230 kt/yr of xylitol and 116 kt/yr of sorbitol are obtained, with an investment adds up to 120.5 M€ for a production cost of 0.25€/kg.

## 7.-Nomenclature

| | |
|---|---|
| a,b,c | Fitting parameters for ammonia recovery column operation |
| d,e | Fitting parameters for xylitol conversion |
| $d_1$, $d_2$, $d_3$ | Fitting coefficients to obtain d parameter |
| $e_1$, $e_2$, $e_3$ | Fitting coefficients to obtain e parameter |
| amonia_ratio | Ratio of ammonia added vs. dry biomass to AFEX pretreatment ($g \cdot g^{-1}$) |
| conc_acid_mix | Acid concentration at pretreatment in weight percentage. |
| $C_i$ | Material cost ($\$ \cdot g^{-1}$ or $\$ \cdot W^{-1}$) |
| $Cp_i$ | Heat capacity of component I (kJ/(kg·ºC)) |
| $D_{i,k}$ | Flow of component I in distillate of column k |
| Dt: | Temperature increment |
| enzyme_add | Ratio of enzyme added to hydrolysis for acid pretreatment as function of the glucan ($g \cdot g^{-1}$ ) |
| $c_{ri}$ | Flow of sugar i in crystal stream (kg/s) |
| $f_{cH2}$ | Flow of consumed hydrogen (kg/s) |
| $f_{cSorbitol}$ | Flow of purified sorbitol (kg/s) |
| $f_{cXylitol}$ | Flow of purified xylitol (kg/s) |
| $f_{di}$ | Flow of sugar i in evaporator feed (kg/s) |
| $l_i$ | Flow of sugar i in solution flow (kg/s) |
| $F_d$: | Feed to multieffect column (kg/s) |
| $\Delta H$ | Reaction enthalpy (kJ/mol) |
| $\Delta H_{form\ i}$ | Formation enthalpy of component i at 25ºC (kJ/kg) |
| $H_{cr}$ | Crystals enthalpy (kW) |
| $H_E$ | Vapor enthalpy (kW) |
| $H_e$ | Condensated vapor enthalpy (kW) |
| $H_{Fd}$ | Feed enthalpy (kW) |
| $H_L$ | Solution enthalpy (kW) |
| $H_S$ | Steam enthalpy (kW) |
| $H_s$ | Condensated steam enthalpy (kW) |
| LoadAmmonia_water | Mass ratio between ammonia and water |
| $m_{(J,\ unit,unit1)}$ | mass flow of component J from unit to unit 1(kg/s) |
| $m_i$ | Molality of sugar i (mol/kg) |
| $K_b$ | Ebullioscopy water constant (0.512 kg/(mol·K)) |
| $K_{isomerization}$ | Isomerization glucose constant |
| P | Pressure (bar) |
| $P_i$ | Prices of component i (€/kg - €/kWh) |
| $P_j$ | Operating pressure of evaporator j (bar) |
| $P_k$ | Pressure of column k |
| $Q_{(unit)}$ | Thermal energy involved in unit (W) |
| $Qb_k$ | Thermal flow in boiler of column k |
| $Qw_k$ | Thermal flow in condenser of column k |
| R | Reflux ration |
| ReactionTime | Reaction time in catalytic reactors CR-1 and CR-2 |
| $T_{(Unit,\ Unit1)}$ | Temperature of the stream from unit to unit 1 (ºC) |
| $Tb_k$ | Temperature in boiler of column k |
| $Tc_k$ | Temperature in condenser of column k |
| time_pret (min) | Time for acid pretreatment |
| T | Operating temperature (ºC) |

| | |
|---|---|
| T_acid | Operating temperature acid pretreatment (°C) |
| T_afex | Operating temperature AFEX pretreatment (°C) |
| $T_{Cr}$ | Operating crystals temperature (°C) |
| $T_{eb}$ | Ebullition temperature (°C) |
| $T_E$ | Vapor overhead temperature (°C) |
| $T_{Fd}$ | Operating feed temperature (°C) |
| $T_L$ | Operating solution temperature (°C) |
| $T_{ref}$ | Operating reference temperature (25 °C) |
| $T_S$ | Operating steam temperature (°C) |
| $T_j$ | Operating temperature in evaporator j (°C) |
| $T_{j+1}$ | Operating temperature in evaporator j+1 (°C) |
| time_pret | Time for AFEX pretreatment (min) |
| water_pret | Ratio of water added to AFEX pretreatment function of the dry biomass ($g \cdot g^{-1}$) |
| $W_{i,k}$ | Flow of component I in residue of column k |
| $W_{(unit)}$ | Electrical power involved in unit (W) |
| $x_i$ | Sugar i solubility (g/100 water – kg/kg water) |
| $X_i$ | Sugar i conversion |
| yield | Yield of the pretreatment / unit |

**Symbols**

| | |
|---|---|
| $\lambda$ | Latent heat steam (kJ/kg) |
| $\eta$ | Separation ratio in column |
| [] | Concentration (mol/L-g/100 ml water-kg/kg water) |

**Appendix**

Wa: Water
$CO_2$ : Carbon dioxide
$CH_{1.8}O_{0.5}N_{0.2}$: Cells
$C_5H_{10}O_5$ : Xylose
$C_5H_{12}O_5$ : Xylitol
$C_6H_{12}O_6$ : Fructose-glucose
$C_6H_{14}O_6$ : Sorbitol
CaO: Lime
$CaSO_4$ : gypsum
$H_2$: Hydrogen
$H_2SO_4$ : Sulfuric acid
$NH_3$ : Ammonia
$O_2$ : Oxygen

**Indexes**

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f

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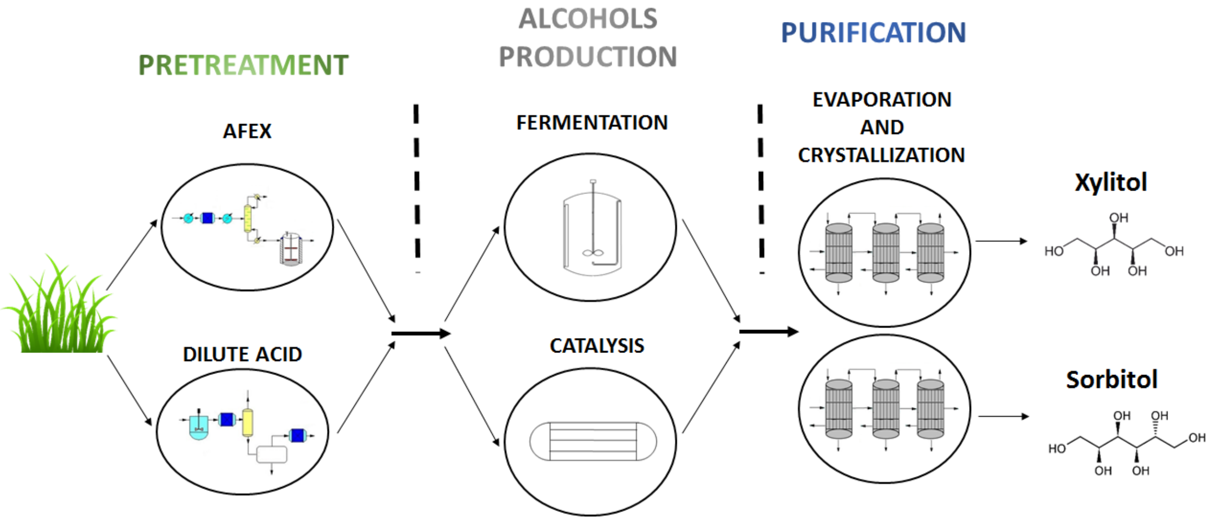

Integrated facility for the simultaneous production of xylitol and sorbitol form lingocellulosic residues.