

Integrated Renewable Production of Sorbitol and Xylitol from Switchgrass

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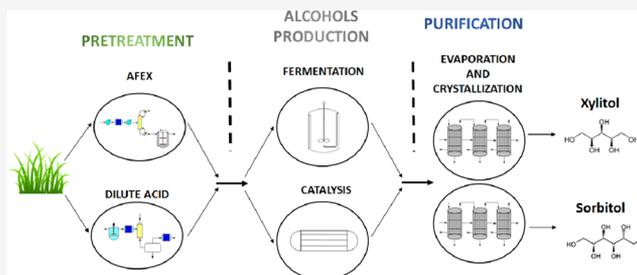
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ABSTRACT: This work deals with the design of integrated facilities for the production of xylitol and sorbitol from lignocellulosic biomass. Xylitol can be obtained from xylose via fermentation or catalytic hydrogenation. Sorbitol is obtained from glucose, but preferably from fructose, and 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 other agricultural and forestry residues. Different pretreatments, such as dilute acid or ammonia fiber explosion (AFEX), for the fractionation of the biomass are evaluated. Next, after hydrolysis, the C5 and C6 sugars are processed separately for which a catalytic or a fermentation stage are considered. Glucose has to be isomerized before it can be processed. Finally, crystallization in a multistage evaporator system is used for purification. The optimization of the system is done by 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 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), which 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 0.25 €/kg products, respectively.



1. INTRODUCTION

The chemical industry is undergoing a transformation toward 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 in the production of energy and chemicals.² While energy and fuels were the first focus of biorefineries design, such as first- and second-generation bioethanol,^{3,4} the valorization of biomass toward platform chemicals and added-value products is part of this new strategy. Lignocellulosic biomass is a promising feedstock as it consists of cellulose, hemicellulose, 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 The hemicellulose building block is xylan, the precursor of xylose that can be converted into furfural⁶ or xylitol among others. Apart from sweeteners, xylitol and sorbitol are considered in the production of dietetic foods to diabetic patients because of the non-insulin-dependent metabolic pathway. They can be used also in pharmaceutical applications (mainly as a carrier), the cosmetics industry (as an emulsion stabilizer), as a moisturizer, texturizer, and softener.⁹ The US Department of Energy^{10,11} lists xylitol and sorbitol as the top 12 high-value-added building block intermediate chemicals that can be produced from renewable biomass resources, while the EU has included them both as part of the

map of potential value chains based on sugars¹² due to the fact that there already exist commercial markets¹³ with the potential to replace petrochemicals¹⁴

The chemical synthesis of sorbitol has been evaluated from glucose via catalytic hydrogenation,^{15,16} or from the fermentation of fructose^{17,18} produced via glucose isomerization.^{19,20} In addition, technoeconomic studies have been performed to evaluate a biorefinery that uses lignocellulosic residues for the production of sorbitol, without considering the use of hemicellulose.²¹ Separately, the yield of xylitol synthesis has been evaluated via xylose fermentation²² as well as hydrogenation.²³ The technoeconomic analysis comparing both synthetic paths has been presented by Mountraki et al.,²⁴ while biorefineries based on sugarcane lignocellulosic materials toward the production of xylitol, citric acid, and glutamic acids have also been presented.²⁵ However, lignocellulosic biomass contains the building blocks for the

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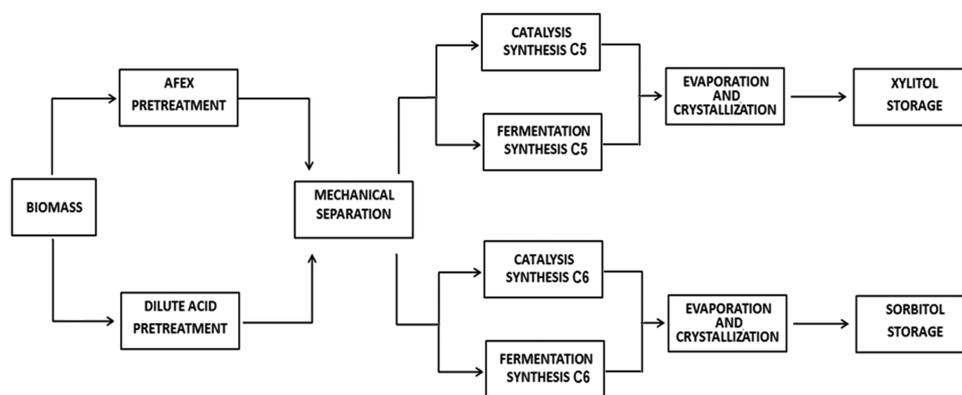


Figure 1. Superstructure for the renewable production of xylitol and sorbitol.

production of both products simultaneously, and so far no biorefinery has considered the production of both.

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 the 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 pretreatments and synthetic routes using 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, and there are a large number of alternative pretreatments.^{2,26–28} The ones more widely used are (1) steam explosion–dilute acid (H_2SO_4) pretreatment^{1,29–31} and (2) ammonia fiber explosion (AFEX).^{27,32,33} Sorbitol can be produced from glucose while hemicelluloses are used for the production of xylitol.⁷ Thus, once the lignocellulosic structure of the biomass is broken down, 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 50 °C. In this case, only xylan is hydrolyzed using an enzyme, xylanase, to promote the degradation. Similar considerations have been used in previous works, as shown by Aristizábal and Gomez.³⁴ Cellulose has to be hydrolyzed at 45–50 °C for 3 days to obtain glucose.^{30,35–37}

Glucose and xylose may follow two different pathways to produce sorbitol and xylitol: fermentation and catalytic synthesis. Xylitol can be produced via fermentation using the bacteria *Candida guilliermondii*,³⁸ and adjusting the operating conditions at 30 °C and 1 bar of pressure with a residence time from 35 h to over 100 h.²⁴ The fermentative production of sorbitol follows two steps: (1) an isomerization stage from glucose to fructose, which is carried out by *Streptomyces* sp. at 70 °C,²⁰ and (2) fructose fermentation to sorbitol. The catalytic production of xylitol is performed in a three-phase

stirred-tank reactor operating at 100–120 °C and 40–60 bar for 60–241 min.³⁹ The reaction uses Ru as a catalyst supported generally over NiO, TiO_2 , activated carbon, or zeotype.^{40–42} Sorbitol production follows a similar route. The reaction is carried out also in a three-phase stirred reactor employing Ru-modified particles as a catalyst.^{16,43,44} The operating conditions are 100–140 °C and 40–60 bar¹⁶ for 60–240 min.

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

3. MATHEMATICAL MODELING

All of the operations in the production of renewable xylitol and sorbitol from switchgrass are modeled with mass and energy balances, experimental yields, thermodynamic and chemical equilibrium, and thumb rules.⁴⁵ To model the pretreatments, surrogate models are developed using data from experiments or rigorous simulations of the units, ammonia recovery, and catalytic xylitol production.

The superstructure is mathematically formulated in terms of temperature, total and component mass flows, and component mass fractions. The components in the system are included in set $J = \{\text{water}, \text{H}_2, \text{H}_2\text{SO}_4, \text{CaO}, \text{ammonia}, \text{protein}, \text{cellulose}, \text{hemicellulose}, \text{glucose}, \text{xylose}, \text{lignin}, \text{ash}, \text{CO}_2, \text{O}_2, \text{cells}, \text{glycerol}, \text{succinic acid}, \text{acetic acid}, \text{lactic acid}, \text{gypsum}, \text{ethanol}, \text{xylitol}, \text{sorbitol}\}$.

3.1. Pretreatment. The main 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 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 to be as follows: 15–20% moisture, 25–40% cellulose, 20–30% hemicellulose, 15–25% lignin, and 5.95% ash. The feedstock is washed and its size is reduced by grinding.^{2,46} The washing and grinding stages are considered only in terms of energy consumption (162 MJ/t)⁴⁶ and cost analysis since they do not change the composition of the feedstock. Next, the two alternative pretreatments, dilute acid pretreatment and AFEX, are analyzed comparing their yield toward structure degradation.^{27,47–50}

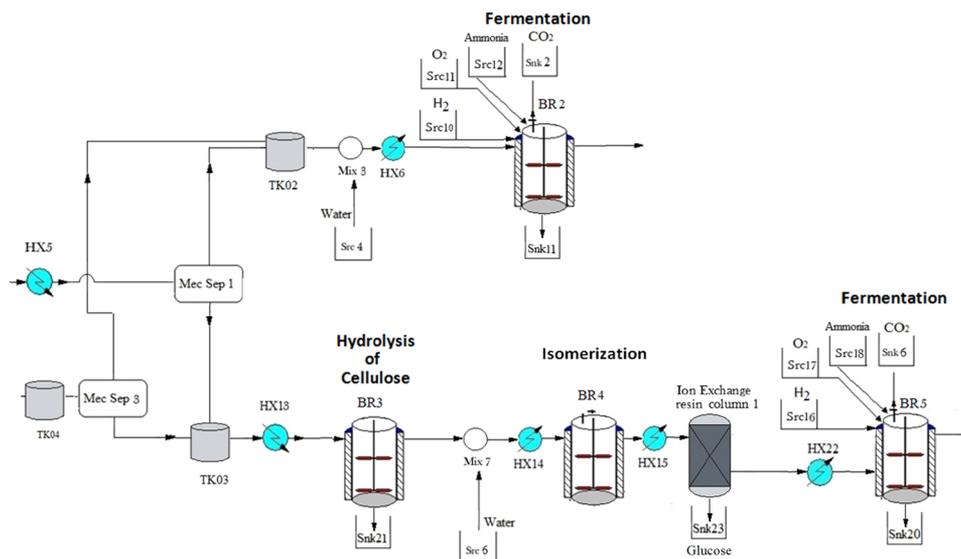
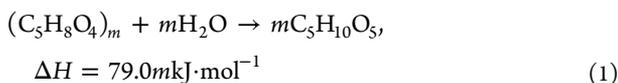


Figure 4. Details of the fermentation pathway.

in Shi's paper,⁵⁷ the surface of response surrogates are developed to estimate the yield of the glucose and xylose released.⁵⁸

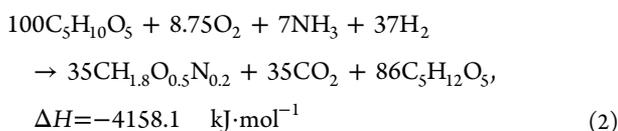
Next, a flash (Flash 1) reduces the water content of the slurry, thereby reducing water consumption and providing energy to the process. The mechanical separation (Mec Sep 2) allows the separation of the slurry. The solid phase is bypassed and the liquid phase is neutralized in Reactor 3 (R03) using solid lime (CaO).^{1,30,59,60} Lime is a low-cost chemical, and the gypsum formed is easily separated from the liquid medium⁶¹ using a filtration stage (Filter 1). The optimal time for this reaction is in the range of 3–10 min. The neutralized liquid stream is mixed adiabatically in Tank 4 with the biomass, and the resulting slurry is sent for hydrolysis. The cellulose needs a further step before it can be broken down into glucose but the xylose is ready to be used.



The complete model and the operating conditions are summarized in the Supporting Information (*Dilute Acid Pretreatment*).

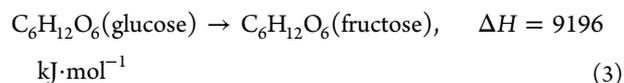
3.2. Xylitol and Sorbitol Production by the Fermentation Pathway. The streams rich in xylose and glucose are mechanically separated using a centrifugation process, Mec Sep-1 and Mec Sep-3, depending on the pretreatment. After this process, two parallel streams are obtained, each of them with a different proportion of sugars; see Figure 4.

The production of xylitol from xylose fermentation is carried out in fermenter BR-2 by the bacteria, immobilized enzyme systems, or the fungus *C. guilliermondii*³⁸ adjusting the operating conditions to 30 °C and 1 bar pressure, with a residence time from 35 to 100 h.²⁴ Heat exchanger (HX) HX-6 and pumps are used to control the temperature and pressure of this operation. The fermentation reaction is as follows



During the process, other secondary reactions may also take place (as shown in eq 2) and are most important, which consume almost all of the xylose reaching a conversion of 92%.²⁴ The unconverted xylose remains in the liquid phase. The hydrogen and oxygen needed are directly fed into the fermenter (Src-10 and Src-11, respectively). Ammonia as a nitrogen source will also be provided (from Src-4) in the form of an aqueous solution to avoid the temperature increase due to the large heat of mixing in BR-2 and to control the input xylose concentration to be in the range of 50–100 g/L.²⁴ In this case, the optimal concentration is 100 g/L because it allows one to use the least amount of diluted water possible.

The production of sorbitol is carried out by fructose fermentation. The pretreatment releases glucose in the form of a dehydrated molecule. Then, glucose is formed by hydrolysis. The next operation consists of the isomerization to fructose²⁰ by *Zymomonas mobilis* in its metabolic route to produce sorbitol.¹⁷ The optimization process of this step consists of optimizing the yield of glucose to fructose. The remaining glucose can be sold to obtain additional revenue but, generally, it is used as a nutrient for the microorganism, avoiding secondary reactions as well. Glucose isomerization is described by eqs 3–5.²⁰



$$K_{\text{isomerization}} = \frac{[\text{Fructose}]}{[\text{Glucose}]} \quad (4)$$

$$X_{\text{isomerization}} = \frac{[\text{Fructose}]}{[\text{Glucose}] + [\text{Fructose}]} \times 100 \quad (5)$$

The key factors in the isomerization are the temperature and the equilibrium isomerization constant, both related, and are shown in Table 1.²⁰

The increase in temperature has a direct effect on the increase in the equilibrium constant of isomerization. Therefore, higher operating temperatures result in higher glucose conversion, but Takasaki²⁰ stipulates temperatures of 70 °C as an upper bound because it is the maximum temperature

The best fitting was developed using the Agustinson equation (eq 10).

$$\frac{\text{ReactionTime}}{X_{\text{xylose}}} = \frac{e}{d} + \frac{\text{ReactionTime}}{d} \quad (10)$$

This linearization model shows a good fit above 50% conversion. However, the operating conditions depend on the pressure and temperature. A two-stage fitting procedure is used to include the effect of pressure and temperature on the fitting parameters d and e , and they are summarized in Table 2.

Table 2. Fitting Parameters d and e

P (bar)	T (°C)	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 determine the effect of the operating conditions on parameters d and e of the linearization model and to create a model that allows predicting the optimal operating conditions for the catalytic hydrogenation of xylose. The fitting of these parameters is obtained based on parabolas, shown in eqs 11 and 12.

$$d = d_1 \cdot (T)^2 + d_2 \cdot (T) + d_3 \quad (11)$$

$$e = e_1 \cdot (T)^2 + e_2 \cdot (T) + e_3 \quad (12)$$

For each pressure, the adjustment coefficients, d_1 and e_1 , d_2 and e_2 , and d_3 and e_3 , corresponding to the quadratic, linear, and independent terms, respectively, are obtained (summarized in Table 3). The fitting coefficients are shown in the Supporting

Table 3. Fitting Coefficients d_1 , d_2 , and d_3

P (bar)	d_1 (bar ⁻²)	d_2 (bar ⁻¹)	d_3
40	0.0015268518	-0.3564497953	21.791809307
50	0.0013628024	-0.3160760678	19.2963948214
60	0.0002761889	-0.0677064946	5.1345819739

Information (Parameters Fitting, Figures S7–S12). The adjustment coefficients d_1 , d_2 , and d_3 are summarized in Table 3.

$$d_1 = -0.0000046128 \cdot (P)^2 + 0.0003987489 \cdot (P) - 0.0070425916 \quad (13)$$

$$d_2 = 0.0010399792 \cdot (P)^2 - 0.0895607578 \cdot (P) + 1.5620137517 \quad (14)$$

$$d_3 = -0.0583319918 \cdot (P)^2 + 5.0003378143 \cdot (P) - 84.8905163696 \quad (15)$$

The coefficient values e_1 , e_2 , and e_3 are summarized in Table 4.

$$e_1 = -0.0008951573 \cdot (P)^2 + 0.0767103691 \cdot (P) - 1.3058206785 \quad (16)$$

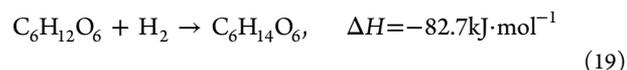
$$e_2 = 0.2025593072 \cdot (P)^2 - 17.2901256531 \cdot (P) + 290.5971371624 \quad (17)$$

$$e_3 = -11.4004523267 \cdot (P)^2 + 968.4617221371 \cdot (P) - 16,022.5819653434 \quad (18)$$

Table 4. Fitting Coefficients e_1 , e_2 , and e_3

P (bar)	e_1 (min/bar ²)	e_2 (min/bar)	e_3
40	0.3303424081	-76.912997503	4475.1631974317
50	0.291804531	-67.5108775881	3899.3733247795
60	0.0742351944	-17.5968962407	1043.4929867889

On the other hand, the stream rich in glucose is directed toward heat-exchanger HX-16, adjusting the temperature between 100–140 °C and the pressure to 40–60 bar¹⁶ before directing it to the catalytic reactor CR-2. The reaction is run for 60–240 min. The synthesis of sorbitol from glucose is carried out in a three-phase stirred reactor employing Ru-modified particles as a catalyst.^{16,43,44} The catalysts based on Ni-Raney allow achieving a high conversion of glucose but have the same disadvantages as the ones for the production of xylitol.



A fresh stream of H₂ 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 excess of H₂ atmosphere 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 profile 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 the data reported on the conversion of glucose (above 99.9%),^{44,60,65} and maximizing the amount of sorbitol produced simultaneously minimizing the costs associated with energy (see Section 3.4).

Two heat exchangers, HX-8- and HX-17, with auxiliary utilities, control the temperature of the streams that are directed to the membrane modules in cases 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 multi-effect evaporators, Evap1-Evap2-Evap3 and Evap4-Evap5-Evap6, for xylitol and sorbitol, respectively; see Figures 6 and 7. The streams coming from the MS-1 and MS-2 membranes, rich in xylitol and sorbitol, are directed toward HX-11 and HX-20 where their temperatures are set depending on the solubility of different sugars (eqs 22–25) to improve the purification process.

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 steam

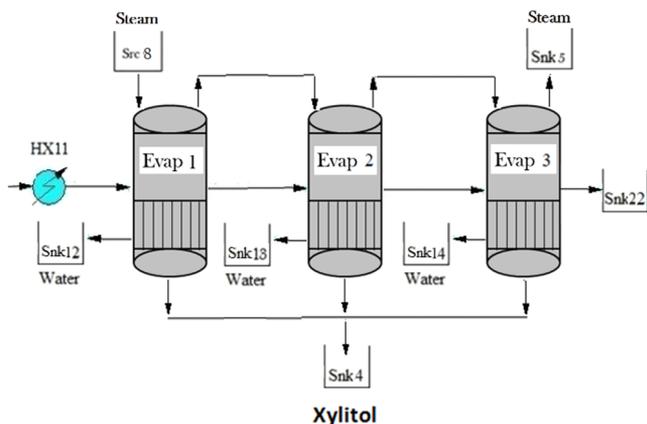


Figure 6. Xylitol purification.

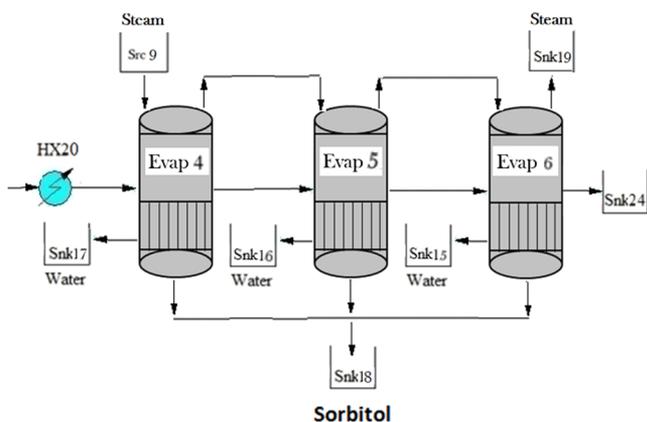


Figure 7. Sorbitol purification.

that is used as a heating agent in the next effect. The mass balance of the solute is as follows⁶⁶

$$F_j \cdot x_{j,f,i} = C_{j,i} + L_j \cdot x_{j,l,i} \quad \forall j \in \{\text{effects}\}, i \in \{\text{sugars}\} \quad (20)$$

$$x_i = \text{solubility of species } i \quad (21)$$

where x is given by eqs 20–25 for each of the sugar and sugar alcohols.

$$x_{\text{xylose}} = 0.0005 \cdot (T)^2 - 0.003 \cdot (T) - 0.9957 \quad (22)$$

$$x_{\text{xylitol}} = 0.2102 \cdot (T)^2 - 6.0031 \cdot (T) + 201.47 \quad (23)$$

$$x_{\text{fructose}} = 0.0016 \cdot (T)^2 - 0.0196 \cdot (T) + 3.1655 \quad (24)$$

$$x_{\text{sorbitol}} = 0.1321 \cdot (T)^2 - 0.1578 \cdot (T) + 166.26 \quad (25)$$

The mass balance of water in the evaporation chamber of each effect is given by eq 26.

$$f_{\text{water}} = \text{vapor}_j + l_{\text{water}} \quad (26)$$

This condition is common for all sets of evaporators because the steam used in each effect is not in direct contact with the sugar solutions. The energy balance for the first effect is given by eq 27

$$H_{Sj} + H_{Ei} = H_{sj} + H_{Ej} + H_{Lj} + H_{C_{rj}} \quad (27)$$

while for the other effects, the balance is as in eq 28.

$$H_L + H_{Ej} = H_{sj} + H_{E_{j+1}} + H_{L_{j+1}} + H_{C_{rj+1}} \quad (28)$$

The enthalpies of the streams are calculated by the components considering enthalpies of formation, crystallization, and solution of the solids. For the rest of the liquid streams, they can be calculated using eqs 29 and 30.

$$H_{F_d} = \sum f_{di} \cdot (\Delta H_{\text{form } i} + \int_{T_{\text{ref}}}^T c_{pi} \cdot dT) \quad (29)$$

where

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

H_E is the enthalpy of the superheated steam since it is generated in a solution where sugar concentration increases.

$$H_E = E \cdot \left(\Delta H_{\text{form } \text{Wa}(\text{liq})} + \int_{T_{\text{ref}}}^{T_{\text{eb}}} c_{p,\text{liq}} \cdot dT + \lambda(T_{\text{eb}}) + \int_{T_{\text{eb}}}^T c_{p,\text{vap}} \cdot dT \right) \quad (31)$$

For the rest of the vapor streams, it can also be calculated using eq 31. H_{cr} is the enthalpy of the crystals and can be calculated by eq 32

$$H_{Cr} = \sum c_{ri} \cdot (\Delta H_{\text{form } i(\text{liq})} + \Delta H_{\text{cryst } i} + \int_{T_{\text{ref}}}^T c_{pi} \cdot dT) \quad (32)$$

The model is formulated so 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.

$$[\text{Sugar}]_i = x_i \quad (33)$$

Equation 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 on the chemical route. The catalytic synthesis process presents almost 100% conversion of xylitol and sorbitol. In this case, xylitol and sorbitol are free from impurities, allowing easier separations. However, fermentation results in 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 recovering them separately without the risk of having impurities. In the case of xylitol, it should be noted that as its solubility is higher than the solubility of xylose, the presence of a certain amount of xylose in solution results in either lower recovery of xylitol or a decrease in its purity.

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

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

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

where K_b is the boiling constant of water (equal to 0.512 kg/(mol K)) and m_i is the molality of each sugar molecule. The pressure of each chamber is given as a function of T_{eb} using the Antoine's equation (eq 36)

$$P_j = e^{(18.3036 - 3816.44/T_{\text{eb}} + 227)} \quad (36)$$

The additional process constraints are given by eqs 37 and 38.

Table 5. Pressure and Temperature for the Pretreatments

	dilute acid-catalysis hydrogenation		AFEX-catalysis hydrogenation		dilute acid-fermentation		AFEX-fermentation	
	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)
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 (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)
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

Table 7. Pressure and Temperature for the Evaporators

		dilute acid-catalysis hydrogenation		AFEX-catalysis hydrogenation		dilute acid-fermentation		AFEX-fermentation	
		P (mmHg)	T (°C)	P (mmHg)	T (°C)	P (mmHg)	T (°C)	P (mmHg)	T (°C)
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				
sorbitol	kg _{steam} /kg _{xylitol}	0.23		0.20		7.17		7.15	
	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	

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

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

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 (NLPs) are solved involving 2700 equations and 3800 variables each. The major decision variables are the operating conditions at the pretreatment reactors, feed ratios and operating temperatures, the operating conditions during the synthesis, the split fraction, and operating pressures and temperatures at the evaporator sets. The last one depends on the yield of each pretreatment and the biomass composition. The model is solved using a multistart optimization approach in GAMS^(R) with CONOPT 3.0 as the preferred solver. The objective function is the maximization of a simplified profit 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)

$$Z = P_{\text{xylitol}} f c_{\text{xylitol}} + P_{\text{sorbitol}} f c_{\text{sorbitol}} - P_{\text{steam}} \sum_i \frac{Q_i}{\lambda} - P_{\text{H}_2} f c_{\text{H}_2} \quad (39)$$

Next, a heat exchanger network is developed⁶⁷ and the economic evaluation is performed to compute production and investment costs.⁶⁸ The production cost involves annualized equipment, chemicals (enzymes, sulfuric acid, CaO, ammonia, and the profit from gypsum), labor, utilities, and raw materials. The costs for utilities are updated from the literature: steam, 19 \$/t; cooling water, 0.057 \$/t; electricity, 1.7×10^{-8} \$/J;⁶⁹ and the base price for biomass: 100 €/t. The estimation of investment is performed with the factorial method.⁶⁸ First, the equipment cost is estimated with the mass and energy balances obtained from optimization. The cost for the equipment such as heat exchangers, fermenters, tanks, distillation column, mechanical separation, filters, and molecular sieves is updated from the values calculated using the correlations developed by the authors; see [Supporting Information](#) of Martín and Grossmann³ and Almendra and Martín.⁷⁰ Next, the equipment cost is calculated as a function of the equipment cost, using factors of 3.15 and 1.4. These factors correspond to the facility processes, fluids and solids for the physical, and total fixed costs.⁶⁸

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

5. RESULTS

The facility is based on a feed of 18 kg/s of biomass, typically used in bioethanol production facilities and biomass processing⁷¹ using switchgrass as a base case.

5.1. Facility Operation. Tables 5–7 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 process requires a higher temperature than AFEX, 180 vs 110 °C, which together with the presence of the acid allows the degrading of a higher amount of hemicellulose to xylose. However, note that the acid can dehydrate sugars into furfural and furans, which are inhibitors for fermentation; we assume that it is not the case here.⁵⁴ AFEX pretreatment requires higher pressure to break down the lignocellulosic structure of the biomass, and an additional stage for the hydrolysis of the hemicellulose that is carried out in a fermenter at 50 °C and 1 bar.

Within the synthesis routes, the catalytic process makes use of high pressures, close to 48 bar, and moderate temperatures, 100 °C or higher. The target of minimizing energy consumption and increasing xylose and glucose conversion allow operations at or near the lower limit of the operating conditions.^{16,39} The fermentation process operates at mild pressure and temperature conditions, typically at 1 bar in all cases, and 30 °C for the xylose and fructose fermentations and 70 °C for the isomerization of glucose to fructose. Fermentation results in obtaining lower sugar conversion rates due to the metabolism of *C. guilliermondii*³⁸ and *Z. mobilis*,¹⁷ larger volumes of feed, and an increase in the processing time.

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, a comparison among the alternatives is performed based on the following ratios: $\text{kg}_{\text{steam}}/\text{kg}_{\text{xylitol}}$ and $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbitol}}$ (Table 7). The catalytic synthesis processes use a significantly smaller amount of steam in the evaporators due to higher concentrations of xylitol and sorbitol. These processes show higher conversions of glucose and xylose. In addition, the fermentation synthesis processes require large volumes of cell cultures, which results in lower conversions of sugars and larger amounts of commercial steam. The difference in the operating conditions is 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 yields of xylitol and sorbitol are higher, which increases 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 fermentation synthesis processes require an appropriate concentration of xylose.³⁸ To achieve this, it is necessary to dilute the stream with water, which is later removed in the evaporators.

Table 8 shows the main operating ratios used to compare the alternative production paths. It can be observed that the yields of xylitol and sorbitol are lower in the fermentation paths due to the lower conversion achieved by the bacterial cultures. The processes with lowest operating to obtain xylitol and sorbitol are designed using the catalytic path. Within the

Table 8. Major Yields of the Alternative Production Paths^a

	dilute acid-catalysis hydrogenation	AFEX-catalysis hydrogenation	dilute acid-fermentation	AFEX-fermentation
X_{xylose}	1	1	0.92*	0.92*
X_{glucose} or X_{fructose}	>0.999 (G)*	>0.999 (G)*	92.9 (F)	0.941 (F)
$\text{kg}_{\text{H}_2}/\text{kg}_{\text{biomass}}$	0.007	0.005	0.001	0.001
$\text{kg}_{\text{H}_2\text{SO}_4}/\text{kg}_{\text{biomass}}$	0.024		0.017	
$\text{kg}_{\text{NH}_3}/\text{kg}_{\text{biomass}}$		1.052		1.052
$\text{kg}_{\text{xylitol}}/\text{kg}_{\text{biomass}}$	0.259	0.187	0.166	0.120
$\text{kg}_{\text{sorbitol}}/\text{kg}_{\text{biomass}}$	0.282	0.231	0.142	0.102
$\text{kg}_{\text{steam}}/\text{kg}_{\text{biomass}}$	0.505	0.587	2.013	1.374
E ($\text{kg}_{\text{CO}_2}/\text{kg}_{\text{biomass}}$)	0.145	0.136	0.296	0.206

^aAbbreviations: F, from fructose; G, from glucose; *indicates from the literature.

catalytic process, the dilute acid pretreatment allows obtaining a higher 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.

The steam consumption in the hydrogenation-based processes is one-third to one-fourth of that consumed in the fermentation processes. However, hydrogen consumption is 5–6 times higher. An environmental index to account for both contributions simultaneously based on the equivalent CO₂ emissions has been computed as follows: eq 40, where EF is the individual environmental factor related to each of the contributions, which is 10.5 kg CO₂/kg H₂⁷² and 0.142 kg CO₂/kg steam,⁷³ respectively. Note that the feedstock is biomass, a carbon-neutral source, and the index is built for comparison purposes among the different alternatives; the results are shown in Table 8. The larger energy consumption in the fermentation-based processes results in higher emissions for both pretreatments. In addition, between dilute acid and AFEX, the lower hydrogen consumption shows a lower impact due to the lower production of xylitol and sorbitol. Note that the emissions related to hydrogen correspond to the ones when it is not produced using renewable resources.

$$E = f_{c_{\text{H}_2}} EF_{\text{H}_2} + f_{c_{\text{steam}}} EF_{\text{steam}} \quad (40)$$

5.2. Economic Evaluation. The economic evaluation is performed for 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 8. Table 9 summarizes the total costs, which increase when the fermentation paths are selected. In general, the fermentation process in continuous operation requires several fermenters operating in parallel. This, together with the need for larger volumes of flows to be treated and larger needs for steam used in the evaporators to concentrate the streams (Tables 7 and 8), results in larger costs. Regarding the pretreatments, AFEX involves higher costs than the dilute acid pretreatment in the case of catalysis hydrogenation as a distillation column is required to recover the ammonia used and an additional stage of hemicellulose hydrolysis, which

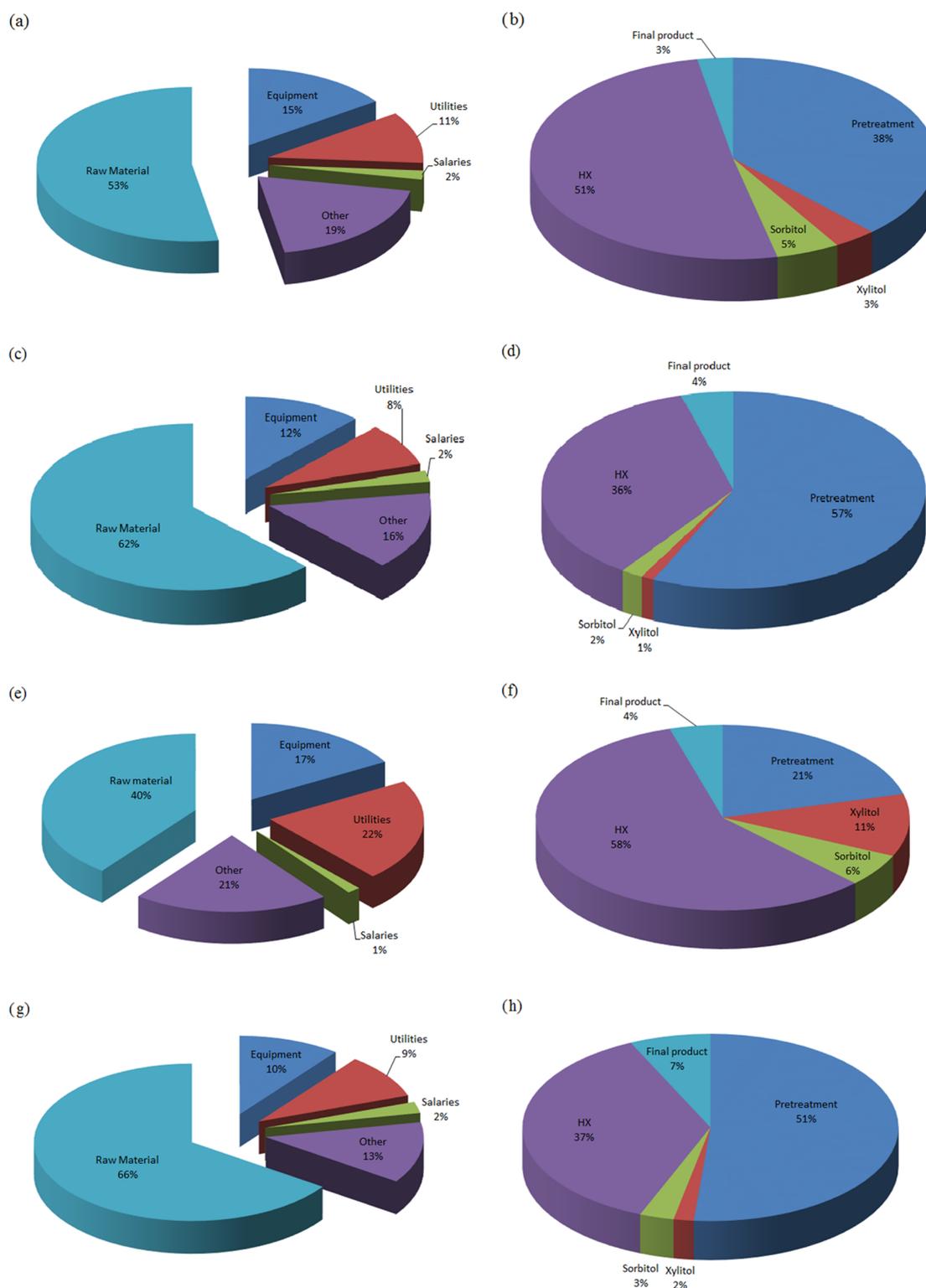


Figure 8. Detailed productions costs and investment costs for AFEX-fermentation (a and b), AFEX-catalytic hydrogenation (c and d), dilute acid-fermentation (e and f), and dilute acid-catalytic hydrogenation (g and h).

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

explains the difference of 57 and 51% in the pretreatment costs between AFEX and dilute acid catalytic hydrogenation (Figure 8d,h). The fermentation paths feature the opposite behavior. This can be explained as follows: the increase in the amount of sugar results in the use of more water to adjust the xylose concentration in the fermenter, requiring more fermenters and a higher 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 pretreatments, respectively (Figure 8b,f). This can also be observed in the percentage of utilities of production costs, reaching 18 and 22% of the total, respectively (Figure 8a,c). From Figure 8b,d,f,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 lowest cost process to obtain xylitol and sorbitol from switchgrass is the one that uses dilute acid as pretreatment and catalytic hydrogenation as a synthetic path.

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 also used to evaluate other typical biomasses such as corn stover, sugar bagasse, wheat straw and forest residues like a birch, pine and spruce, hybrid poplar. The results are summarized in Table 10 with the composition of each biomass. The composition of water has a direct effect on the steam ratio used; the higher the amount of water, the higher the amount of steam required to adjust the xylitol and sorbitol concentration. Furthermore, the increase in the fraction of water implies an 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. The environmental index for all of these biomasses remains in the range of 0.130–0.150 kg CO₂/kg_{biomass} because of the use of the same production process. The fermentation paths used increase those values to above 0.20 kg CO₂/kg_{biomass}. In general, the amount of lignin plays a fundamental role in the costs since it is the biomass that cannot be transformed into products. In addition, an increase in the lignin content implies a higher energy consumption in the pretreatment and an increase in production and investment cost, in spite of the possible production of energy out of it. 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.

5.3.2. Biomass Design. As a complementary objective of this work, instead of using a fixed biomass composition, belonging to a lignocellulosic feedstock such as switchgrass, the optimal flowsheet is used to determine the best composition within the typical ranges of hemicelluloses, cellulose, and lignin for simultaneous production. The resulting composition is compared with a database to determine the most suitable biomass. In this way, the resulting biomass composition corresponds to 15% water, 20% cellulose, 40% hemicellulose, 15% lignin, 5% ash and 5% others. One that fits the best is sargassum algae (*sargassaceae*) with a composition of 20.48%

Table 10. Major Yields, Investment, and Production Costs for Different Biomasses^a

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)	E (kg _{CO₂} /kg _{biomass})
	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	0.145
corn stover	16.95	41.05	31.39	6.34	4.27	16.3	111.7	0.220	0.323	0.361	0.023	0.009	0.386	25,663	0.146
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	0.140
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	0.008	0.353	97,973	0.134
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	0.008	0.347	99,421	0.135
hybrid poplar	6.91	50.80	26.20	15.50	5.90	18.4	121.5	0.213	0.270	0.447	0.022	0.009	0.357	57,374	0.144
sugar bagasse	7.00	41.00	30.10	21.20	7.00	19.4	125.5	0.230	0.310	0.361	0.022	0.008	0.361	77,889	0.140
wheat straw	8.43	40.26	30.56	16.52	4.23	18.5	121.5	0.228	0.315	0.354	0.022	0.008	0.364	61,446	0.140

^aAbbreviations: W, water; C, cellulose; HC, hemicellulose; L, lignin; A, ash.

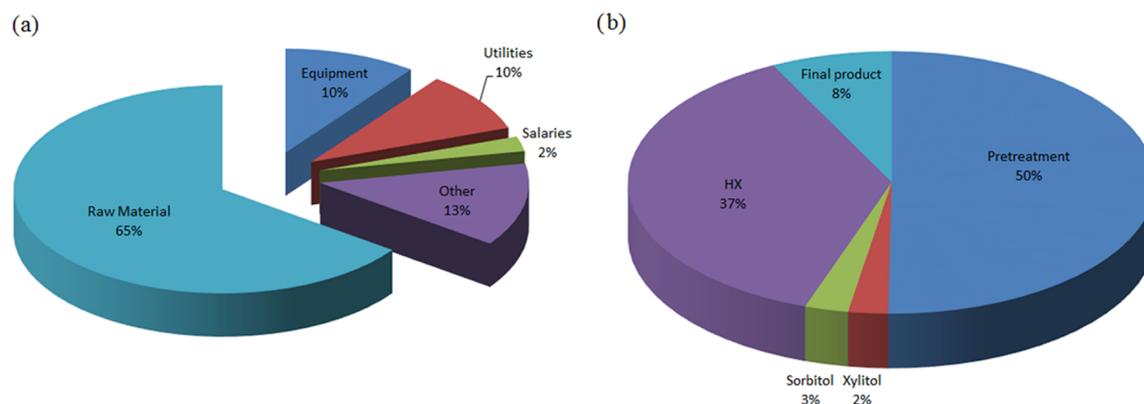


Figure 9. Dilute acid-catalytic hydrogenation free composition: productions costs (a) and investment costs (b).

cellulose and 43.19% hemicellulose. The production and investment costs for this biomass are 18.4 M€/yr (0.25 €/kg) and 120.5 M€, respectively. The breakdown in the costs is shown in Figure 9. Table 11 reports the major values for switchgrass and sargassum algae with slightly better values for the latter.

Table 11. Comparison of Investment and Production Costs 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 yield similar values. The larger difference between them is the ratio of xylitol and sorbitol produced per kg of biomass. The amount of xylitol and sorbitol produced are 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 obtained, respectively. The difference in the market prices of xylitol and sorbitol (3900 and 650 \$/ton)⁷⁴ suggests choosing a larger quantity produced of the product with a higher selling price. However, the environmental impact assessment plays an important role because it allows determining the process with the lowest CO₂ emissions, and therefore, the one that uses the least amount of hydrogen and steam. Thus, the key parameters are the larger amount of xylitol produced per kg of biomass and the environmental index. The differences also explain the choice of sargassum algae as the best biomass, and not the corn stover (Table 12).

6. CONCLUSIONS

Xylitol and sorbitol production from the 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 modeled using first principles and surrogate

Table 12. Comparison of Xylitol and Sorbitol Production among 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
<i>E</i> (kgCO ₂ /kg _{biomass})	0.145	0.141	0.146

models for each of the operations. The selected option is dilute acid as the pretreatment and catalytic hydrogenation as the 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 depending on its composition, as long as the models for the pretreatments are valid. Within the biomasses considered, 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 design of the optimal biomass was performed. Among all of the 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 the existing biomass and provides a lower environmental index. 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 the sargassum algae (*sargassaceae*) biomass. For this biomass, 230 kt/yr of xylitol and 116 kt/yr of sorbitol are obtained, reaching an environmental factor of 0.141 kg CO₂/kg biomass with an investment of up to 120.5 M€ for a production cost of 0.25 €/kg. Further validation of the process at the pilot plant is necessary before actual industrial production using the concepts presented in this work.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c00397>.

Data on the development of models and fittings; results on the break down of costs for different biomasses; operating variables for AFEX pretreatment and dilute acid pretreatment; xylitol and sorbitol production by the fermentation pathway (PDF)

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Notes

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■ NOMENCLATURE

a, b, c	fitting parameters for ammonia recovery column operations
d, e	fitting parameters for xylitol conversion
d_1, d_2, d_3	fitting coefficients to obtain d
e_1, e_2, e_3	fitting coefficients to obtain e
ammonia_ratio	ratio of ammonia added vs dry biomass to AFEX pretreatment (g/g)
conc_acid_mix	acid concentration at pretreatment in weight percentage
C_i	material cost (\$/g or \$/W)
C_{p_i}	heat capacity of component i (kJ/(kg·°C))
$D_{i,k}$	flow of component i in distillate of column k
D_t	temperature increment
enzyme_add	ratio of enzyme added to hydrolysis for acid pretreatment as a function of the glucan (g/g)
E	environmental index (kg CO ₂ /kg biomass)
EF_{H_2}	environmental factor for hydrogen (kg CO ₂ /kg H ₂)

EF_{steam}	environmental factor for steam (kg CO ₂ /kg steam)
c_{r_i}	flow of sugar i in the crystal stream (kg/s)
fc_{H_2}	flow of consumed hydrogen (kg/s)
fc_{sorbitol}	flow of purified sorbitol (kg/s)
fc_{xylitol}	flow of purified xylitol (kg/s)
f_{d_i}	flow of sugar i in the evaporator feed (kg/s)
l_i	flow of sugar i in the solution flow (kg/s)
F_d	feed to multieffect column (kg/s)
ΔH	reaction enthalpy (kJ/mol)
$\Delta H_{\text{form } i}$	formation enthalpy of component i at 25 °C (kJ/kg)
H_{cr}	crystal enthalpy (kW)
H_E	vapor enthalpy (kW)
H_e	condensed vapor enthalpy (kW)
H_{F_d}	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
$m_{(J, \text{unit}, \text{unit } 1)}$	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))
$K_{\text{isomerization}}$	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
$Q_{(\text{unit})}$	thermal energy involved in unit (W)
Q_{b_k}	thermal flow in boiler of column k
Q_{w_k}	thermal flow in condenser of column k
R	reflux ratio
ReactionTime	reaction time in catalytic reactors CR-1 and CR-2
$T_{(\text{Unit}, \text{Unit } 1)}$	temperature of the stream from unit to unit 1 (°C)
T_{b_k}	temperature in the boiler of column k
T_{c_k}	temperature in the condenser of column k
time_pret (min)	time for acid pretreatment
T	operating temperature (°C)
T_{acid}	operating temperature in acid pretreatment (°C)
T_{afex}	operating temperature in AFEX pretreatment (°C)
T_{Cr}	operating crystal temperature (°C)
T_{eb}	boiling temperature (°C)
T_E	vapor overhead temperature (°C)
T_{F_d}	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/g)
$W_{i,k}$	flow of component i in the residue of column k
$W_{(\text{unit})}$	electrical power involved in the 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

λ	latent heat steam (kJ/kg)
η	separation ratio in the column
[]	concentration (mol/L-g/100 mL water-kg/kg water)
Wa	water
CO ₂	carbon dioxide
CH _{1.8} O _{0.5} N _{0.2}	cells
C ₅ H ₁₀ O ₅	xylose
C ₅ H ₁₂ O ₅	xylitol
C ₆ H ₁₂ O ₆	fructose–glucose
C ₆ H ₁₄ O ₆	sorbitol
CaO	lime
CaSO ₄	gypsum
H ₂	hydrogen
H ₂ SO ₄	sulfuric acid
NH ₃	ammonia
O ₂	oxygen

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