Small-sized biorefineries as strategy to add value to sugarcane bagasse

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ABSTRACT

Small-sized biorefineries are not capital intensive and have lower transportation cost, lesser movements of liquid and solid streams, and lower heat transfer problems than high-sized ones. In this work, different scenarios were investigated in order to determine technical and economic viability of different processes to produce valuable products from sugarcane bagasse by small-sized biorefineries. Different alternatives were evaluated, as furfural and xylitol production from hemicelluloses, as well as energy generation and medium-density fibreboard (MDF) production from the residual solid after hemicelluloses hydrolysis. Experimental data obtained by the authors in previous works were used for pretreatment steps, and updated literature data was used for the other processes. A simplified kinetic model was developed for the extraction of xylose, and unit operations processes were selected and simulated. The most profitable option was determined for hemicelluloses use. In addition, costs and benefits that could be obtained exploiting the residual solid feedstock were estimated. The economic evaluation shows that recovery periods are extensive in both scenarios. However, optimization of different steps as liquid to solid ratio of pretreatment, evaporation, or fermentation, could represent attractive and innovative alternatives in order to reduce the recovery periods of capital costs.

1. Introduction

The worldwide demand for fuels and chemicals, the decrease of petroleum reserves, and the polices of reduction of greenhouse gas emissions, are encouraging the development of non-petroleum based products (Giuliano et al., 2014). Lignocellulosic biomass, such as agricultural residues (e.g., corn stover, and sugarcane bagasse), herbaceous crops, forestry wastes, wood, wastepaper, and other lignocellulosic wastes are potential feedstocks for fuels and chemical products (Wyman, 1994). This biomass consists mainly of cellulose, hemicelluloses and lignin, and the conversion of these materials to higher value products requires of the fractionation processes to extract its components (Wyman, 1994).

In the last decade, the number of papers and patents concerning biorefining increased from less than 5 in 2001, to over 160 in 2008 (Zondervan et al., 2011). The typical biorefinery scenario is based on the extraction of sugars and byproducts to produce cellulosic ethanol and fuels to generate steam and electricity (Zhang, 2008a). However, numerous products can be obtained from lignocellulosic materials depending of its components. In lastyears, local products are valued above

commodities, because they are more sustainable and could be sold for higher and/or more constant prices.

The determination of the optimal scale of operation for a specific process requires the optimization and integration of the processes to identify the most promising pathways to increase the profitability of biofuels and bioproducts (Giuliano et al., 2014). Large-scale biorefineries may have advantages in the production of commodities. In this case, transportation cost of raw materials and products can have a major impact in overall costs, depending on the transportation distance. One of the main incentives for the installation of small-scale biorefineries is the reduction in transportation costs, although studies of logistics are always needed. The transportation costs can be reduced by a local pre-processing because of raw materials bulk and high water content.

In small-scale processing, technologies can be less expensive, the costs of raw materials can be irrelevant, since farmers can be both producers and processors, and rural employment can increase. Other advantages are less risk in investment, so it is easier to get investors for new technologies on a small scale, which makes faster innovations possible. Large projects have greater risks whence required investigations and intellectual property protection before its execution. It is easier to invest for new technologies on a small scale, which makes faster innovations possible. Small biorefineries produce fewer amounts of products, which avoid the overloading of the market in which prices would decrease and smaller increases in productivity are more easily absorbed. Since in an integrated biorefinery there are a very large number of available process configurations, feedstocks, and products, it is necessary to develop a systematic methodology that handles (Bruins and Sanders, 2011; Bao et al., 2011).

The feasibility of small-scale process increase when techniques in which a lot of heat exchange is avoided, e.g. biotechnology. This reduces or prevents the need of extreme industrial conditions of temperature, pressure and corrosion formation (Bruins and Sanders, 2011).

There is a growing trend in the last years towards a more efficient use of renewable agro-industrial wastes, including sugarcane bagasse (Pandey et al., 2000). Sugarcane is one of the most important energy crops in tropical countries such as Brazil and India (Moncada et al., 2014). The main purpose of sugar cane is the production of different qualities of sugar (MECON, 2010), but this industry generates 270–280 kg of bagasse per ton of harvested cane (50% moisture). Brazilian sugarcane harvest was estimated in 629.0 millions of tons in 2009 (De Freitas Branco et al., 2011) and approximately 654 million tons in 2015–2016 (CONAB, 2015), generating more than 160 million tons of sugarcane bagasse. In Argentina, bagasse from sugarcane is one of the most important agro-industrial wastes. An annual output of 19,000 million tons of sugarcane per year was estimated in 2010, being distributed in the provinces of Tucuman, Jujuy, Salta, Santa Fe, and Misiones.

Sugar mills only operate during harvesting, whence the seasonality and storage of bagasse cause problems related with its degradation. Most of the bagasse is currently used as solid fuel in sugar mills and ethanol distilleries; however, it has been demonstrated that the modernization of the boilers and the optimization of steam usage could satisfy the energy requirements of the plants with about 50% of the produced bagasse (Rocha et al., 2012). In this framework, biorefineries are considered as promising processes to convert this lignocellulosic biomass not only into biofuels, but also into added-value chemicals (Giuliano et al., 2014).

Sugarcane bagasse is composed of 43% cellulose, 21–23% lignin, 25–32% hemicelluloses (mainly xylans) and minor amounts of organic extractives and inorganic compounds (Rocha et al., 2012; Vallejos et al., 2012). Xylans polymers from hemicelluloses can be converted to numerous byproducts with different added values as xylose syrup, furfural, xylitol, furan compounds, and furan polymers (Zhang, 2008b). Equipment and process lines to produce xylose syrup and xylitol are similar to those used in sugar mills (mainly, evaporation and crystallization processes). Additionally, xylose (sugar) and xylitol (sweetener) are analogous products to those produced in the sugar mill. In this case the interest is to consider the alternative to convert a part of sugar mill in a small-sized biorefinery in the time between harvests of sugarcane. The residual solids of the process of hemicelluloses extraction can be used to produce energy to attend the energy demands of the plant and/or local power net, whereas, particleboards and fiberboards (medium-density fibreboard (MDF), high-density fibreboard (HDF), etc.) (Papadopoulou et al., 2014), and other value-added products from lignin and cellulose if there is a surplus.

Xylose is the cheapest pentose, with possible application as secondary products, food additives, and detergents after esterification. Xylose can be used also as a sweetener in the form of crystalline powder. The principal derivatives of xylose are xylitol and furfural. Approximately 25,000 t of xylose were produced worldwide in 2004 (Kamm et al., 2008). Syrup prices are relative low to other products derived from hemicelluloses, prices ranging from 0.4 to 1.0 USD/kg (Dávila et al., 2014; Alibaba, 2015).

Furfural is the key derivative of xylose with a broad spectrum of industrial applications in plastic, pharmaceuticals, and agrochemical products (Mamman et al., 2008) such as fungicide, adhesives, flavor compound, and precursor for other products (furfuryl alcohol, tetrahydrofuran and others) (Win, 2005). Furfural is been produced commercially from the hemicellulosic fraction of biomass and it has been considered as one of promising commodity bio-based chemicals (Werpy and Petersen, 2004). The world production of furfural has increased in the last few years due to green chemical initiatives in various industries, being actually around 430,000 t per year (Raman and Gnansounou, 2015). Furfural price is around of 1.0–1.7 USD/kg (Kelloway and Daoutidis, 2013; Win, 2005). Sugarcane bagasse is one of the best feedstock for furfural production because of its high xylans content (WB&TS, 2006). Unlike the conventional furfural production, in which the biomass is hydrolyzed to extract the pentoses, that are dehydrated to furfural in a single stage process (Raman and Gnansounou, 2015), biorefinery approach is to convert hemicelluloses, cellulose, and lignin, in added value products (Raman and Gnansounou, 2015).

Xylitol is used as food sweetener and as moisture retaining agent in pharmaceutical and cosmetic products (De Albuquerque et al., 2014). Its broader application is currently in products such as tooth paste, gum, mouthwash, nasal spray, among others (De Freitas Branco et al., 2011). Xylitol avoids and combats dental caries (Mäkinen, 2000), and it can be consumed by diabetics because it does not require insulin for its metabolism (Grillaud et al., 2005). Xylitol production is expanding in a global level (Kelloway and Daoutidis, 2013), with a strong global demand of more than 125,000 t per year (De Albuquerque et al., 2014). Depending the final product (pharmacies, supermarkets, etc.), prices are about

5–20 USD/kg (De Albuquerque et al., 2014; Leathers, 2003; Kelloway and Daoutidis, 2013; Jeaidi and Stuart, 2011).

The aim of this work was to evaluate the feasibility of a small-scale biorefinery based on sugar cane bagasse for the production of three different chemical products (furfural, xylitol and xylose syrup) from the pretreatment liquor, and the production of MDF fiber boards or electricity generation from the solid residual fraction. A model for a small-sized biorefinery was developed, determining the better scenario based on market prices of the products, production costs and estimation of the payback period for the selected scenario.

2.   Methods

2.1.   Raw material and hydrothermal treatment

Sugar cane bagasse was supplied by a local mill (San Javier Sugar Mill, Misiones, Argentina). Bagasse pith was removed in two stages. In the former, bagasse was wet-depithed to break its structure in a Bauer disc refiner (plate gap of 0.01 in.), after which the bagasse pith was removed by screening, using a plate with 2 mm wide slits (Wenmber). Finally, depithed bagasse was centrifuged and preserved in a refrigerator. The factors of hydrolysis were used to convert xylose and furfural to xylans (132/150 and 96/132, respectively).

Samples of liquor were obtained at different times of hydrothermal treatment, and the content of organic compounds was determined. This samples were characterized by the determination of sugars content (glucose, xylose, and arabinose) and degrading products: furfural, 5-hydroxymethilfurfural and organic acids (formic and acetic), according to Technical Report NREL/TP-510-42623 (January 2008) "Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples", National Renewable Energy Laboratory. The structural carbohydrates in the raw material and in the pretreated solid (glucans, xylans, arabans and acetyl groups) were determined following the Technical Report NREL/TP-510-42618 (April 2008) National Renewable Energy Laboratory. More details can be found in Vallejos et al. (2015b).

2.2.   Definition of scenarios

This study assessed three scenarios as strategy to add value to sugarcane bagasse in small-sized biorefineries. A block flow diagram for the proposed processes involved for sugarcane bagasse hemicelluloses conversion is showed in Fig. 1. The proposed scenarios produce three different high add value products from xylose: xylitol, xylose syrup and furfural. The residual lignocellulosic material is used to produce energy for internal consumption, or it is sold to the local electrical network.

Pressurized hot water at different times and temperatures is used for the removal and selective degradation of the xylans present in the bagasse by autohydrolysis. After the pre-treatment, the solid fraction (mainly cellulose) is filtered to separate the liquid fraction (spent liquor), rich in xylo-oligomers and sugars derived from hemicelluloses (xylose and arabinose). Autohydrolysis treatment is the same for all products, and posthydrolysis treatment is the same for xylose syrup and xylitol. This study develops a simplified kinetic model for the autohydrolysis process of hemicelluloses from the experimental data obtained by Vallejos et al. (2015b). Changes in the composition of the bagasse during the
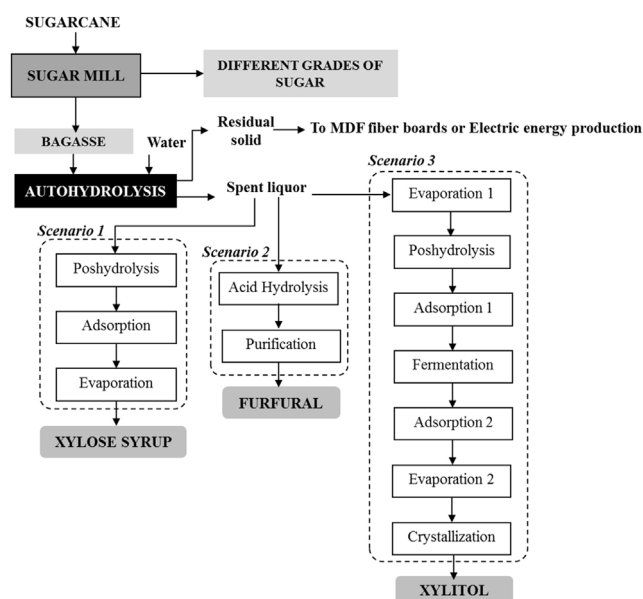

Fig. 1 – Simplified process block flow diagram for the three studied scenarios.

autohydrolysis were taken into account to design and optimize the conversion processes from hemicelluloses to xylose. Kinetic models have been applied to describe autohydrolysis process for different treatment conditions.

The kinetics of the hydrolysis reaction for extraction of hemicelluloses from sugarcane bagasse using diluted acid has been widely studied because of its high reaction rates and high extraction yields (Rodríguez-Chong et al., 2004; Aguilar et al., 2002; Gámez et al., 2006). The model proposed in this study is an adaptation of the irreversible first-order model developed by Saeman (1945), designed for the acid hydrolysis of cellulose from douglas fir wood, which predict the formation of glucose from cellulose and its degradation. The general model of Saeman can be applied to other homopolymers where the monomer is sequentially released and degraded (Rodríguez-Chong et al., 2004). This kinetic model was used to predict the autohydrolysis of xylans to xylose (oligomer of xylans + monomer) which is degraded to furfural and other degradation products (Eq. (1)).

$$Xx \xrightarrow{k_h} X \xrightarrow{k_1} S \tag{1}$$
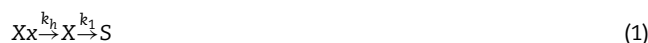
where Xx is the xylans in bagasse (wt.%), X is the oligomers and xylose in spent liquor equivalent to xylans (wt.%), S is the furfural equivalent to xylans in spent liquor (wt.%), wt.% is the weight % based on oven dried bagasse.

Kinetic constants k_h and k_1 were determined using Solver of Apache OpenOffice Calc 4.1.1, by minimizing the sum of the square derivations between experimental and calculated data. Activation energies Ea and $\ln(k_o)$ for the kinetic reactions were calculated from the Arrhenius equations (Eqs. (2) and (3)). The differential equations were from the autohydrolysis model reaction of Eq. (1), were integrated to express analytically the xylans content in the spent liquor, Eq. (4).

$$k = k_0 \cdot e^{-E_a/RT} \tag{2}$$

$$\text{Ln}\,(k) = \text{Ln}\,(k_o) - \frac{E_a}{R}\frac{1}{T} \tag{3}$$

$$X = X_O e^{-k_1 t} + X_{Xo} \frac{k_h}{k_1 - k_h} (e^{-k_h t} - e^{-k_1 t}) \qquad (4)$$

where X is the concentration of xylans in the spent liquor for t (h). X_O is the initial xylans content in the spent liquor; and X_{xo} is the initial xylans content in the bagasse. GAMS Software (CONOPT solver) was used to optimize the autohydrolysis conditions and to determine the temperature and time for maximum extraction of xylans with minimal energy demand.

Although Vallejos et al. (2015b) have used a liquid–solid ratio of 14:1 to ensure a better diffusion of components in the kinetic study, a liquid–solid ratio of 7:1 was adopted in this study to calculate the liquid flow streams. This last value is more reasonable in technical and economic terms, and it was assumed that the diffusion of components during autohydrolysis is not affected.

2.2.1. Scenario 1. Xylose syrup production

After the autohydrolysis treatment, the solid fraction is filtered to separate the spent liquor, rich in xylo-oligomers and xylose. The conversion of the residual solid was described in Section 2.2. The hot spent liquor is pumped to a pressurized reactor where the post-hydrolysis to convert xylo-oligomers to xylose is performed at 120 °C for 60 min and 3% of H_2SO_4. The spent liquor is neutralized in a stirred tank by adding $Ca(OH)_2$, forming gypsum salt ($CaSO_4 \cdot 2H_2O$). Low solubility of gypsum in water facilitates its almost complete separation by filtration (>90%). The detoxification of spent liquor is performed in two adsorption stages. In the first stage, activated carbon columns (concentration of 32 g/L, apparent density of 380 kg/m³, and minimum iodine number of 1000 mg/g) allow to remove HMF, furfural and 90% of phenolic compounds as indicated by Fatehi et al. (2014) and Vallejos et al. (2015a). In the second stage, a sequential set of three ion exchange columns formed by an adsorptive, a strong base anion exchange resin, and a weak acid cationic exchange resin, were selected to simulate acetic acid and formic acid removal, because these acids and other inhibitors (anionic and cationic compounds) remain in the spent liquor after the active carbon treatment (Martínez et al., 2007).

A falling film evaporator system was selected for the last step because it is extensively used in the sugar industry to concentrate sugar solutions (Fatehi et al., 2014; Geankoplis, 1998). The boiling point elevation of each effect was estimated with a table of sugar concentrations (Kern, 1999).

2.2.2. Scenario 2. Furfural production

The furfural production includes three stages: autohydrolysis of bagasse, dehydration of xylose and distillation of furfural. Autohydrolysis was described in item 2.1. The conversion of xylose to furfural is performed by acid hydrolysis with H_2SO_4. The conversion conditions were established on the basis of a study carried out by Montastruc et al. (2011).

Furfural-water mixture is separated by azeotropic distillation (Hoydonckx et al., 2007). A mixture of approximately 30% of furfural is obtained as the distillate of the first distillation column. This cooled distillate is sent to decanters, where furfural is separated spontaneously into a furfural-poor and a furfural-rich phases. Liquid–liquid extraction is possible because the limited solubility of furfural in water (8.3 wt.% at 20 °C). The boiling point of furfural is 161.7 °C at 1 atm., whilst that of the azeotrope is 97.9 °C, so both

columns operate at 98 °C (Montastruc et al., 2011). The H_2SO_4 is sent to recover for recycle and reuse in further hydrolysis using ion-exchange column with the conditions established by (Kumar et al., 2015) (not included in this study).

2.2.3. Scenario 3. Xylitol production

The xylitol production consists of the following stages: autohydrolysis of bagasse, concentration of spent liquor, acid post-hydrolysis, removal of inhibitors by adsorption, fermentation of xylose to xylitol, and xylitol recovery by crystallization. Autohydrolysis, post-hydrolysis and detoxification of spent liquor were described in Sections 2.1 and 2.1.1, respectively.

Spent liquor is concentrated in a falling film evaporator system to 100 g/L of xylose before the post-hydrolysis (Fatehi et al., 2014; Geankoplis, 1998). The boiling point elevation of each effect were estimated as usual (Kern, 1999). Evaporation under vacuum can remove 98% of furfural from spent liquors (Rodrigues et al., 2001). The post-hydrolysis process conditions to convert all polymers to monomers were the same as for xylose syrup, (conversion of xylans to xylose 94%).

The fermentation conditions (temperature, nutrient concentrations, aeration and pH) of the detoxified spent liquor having 100 g of xylose/L, were selected from Ping et al. (2013). *Candida tropicalis* yeast is the inoculum to ferment the xylose to xylitol. Inoculum is prepared in a stirred batch fermenter and after transferred to a larger fermenter at 5 g cell yeast/L. The fermentation of xylose is performed at 35 °C, pH 5–7 for 40 h (Ping et al., 2013).

After fermentation, it is necessary to remove cell yeast, nutrients, and other impurities from fermentation broth. In this study, cell yeast separation and recovery to be recycled to fermentation process, are performed by membrane filtration (Kwon et al., 2006). Nutrients and other impurities in fermentation broth are removed by activated charcoal columns (20 g/L) (Misra et al., 2011; Sampaio et al., 2006; Gurgel et al., 1995). This purification stage is necessary to remove color and odor (Fatehi et al., 2014).

A cost effective, efficient, easy, and less time consuming procedure using activated charcoal treatment followed by concentration (using falling film evaporators) and crystallization was selected. The crystallization of xylitol occurs at temperatures lesser than −10 °C; above this temperature no crystallization occurs [10]. Selected crystallization conditions varied from −20 °C to 8 °C in 4 cycles.

2.3. Conversion of the residual solid

2.3.1. MDF fiber board and electric energy productions

The processes to produce MDF were adapted from Taupier and Bugallo (2000). The residual solid is treated with saturated steam (160–180 °C), and it is pressurized refined to obtain a homogeneous size fibrous material. This material is mixed with urea formaldehyde resin (8–10%) and molten paraffin. The mixture is dried by flash drying to 8–12% of moisture. Hot pressing processes is used to MDF formation, applying pressure and temperature for a short period to obtain the board (Taupier and Bugallo, 2000).

The residual solids from autohydrolysis are combusted to produce high-pressure steam for electricity generation. The steam turbine turns a generator that produces AC electricity (Humbird et al., 2011).

2.4. Mass and energy balances, and economic analysis

For the mass balance, the main flows of solid and liquid streams (raw material, water and reagents) of the different processes and operations, and the main reagents involved in the different processes (H_2SO_4, $Ca(OH)_2$ and others) were taken into account. The flow rate of some operations has been calculated based on yields from the literature. Energy consumption was calculated considering the energy to heat and to maintain the temperature of the different processes.

The economic analysis was performed following the methods of chemical engineering for plant design, and economics analysis (Pham et al., 2012; Couper et al., 2004; Peters and Timmerhaus, 1991; Sadhukhan et al., 2014). The cost and prices of equipment and products were collected from different sources (journals, books, websites as matche.com, alibaba.com, mercadolibre.com) and investment costs (direct and indirect) were estimated. The proposed scenarios to produce xylose, furfural and xylitol were compared with Apache OpenOffice Calc 4.1.1 and cash flows were determined in order to analyze the different scenarios.

3. Results and discussion

3.1. Autohydrolysis process

The chemical composition of this material (as a percentage by weight on oven-dry bagasse, % o.d.b.) involved: 43.1% glucans, 23.8% xylans, 1.7% arabans, 1.7% acetyl groups, 21.3% lignin, 2.1% extractives in alcohol-benzene, 2.7% extractives in hot water and 1.5% of ashes.

The differential equations from the autohydrolysis model reaction of Eq. 1 were integrated to express analytically the xylans content in the spent liquor (oligomers + xylose equivalent) as function of time. The values of the kinetic constants k_h and k_1 (h^{-1}), E_a and $\ln(k_{oi})$ are shown in Table 1.

These parameters were used to determine the optimum temperature and time for the maximum extractions of xylans with a minimal energy demand. The optimum temperature and time were 162 °C and 119 min (1.99 h), respectively. For these conditions, xylans (oligomers + xylose) in the spent liquor are 18.3 wt.% of (77 wt.% of initial xylans content in bagasse).

3.2. Mass and energy balances

The characteristics of the products used for the evaluation of the different scenarios are described below. Gypsum recovered in a set of filter presses is a low value by-product (8 USD/MT), which can be sold to farmers as fertilizer and soil conditioner (Fatehi et al., 2014). The post-hydrolysis yield to convert xylo-oligomers to xylose was supposed to be 94% (Vallejos et al., 2015b). The detoxified spent liquor is evaporated to achieve a xylose concentration of 400 g/L (commercial grade

syrup). Furfural with 99% purity is obtained by distillation of the furfural-rich mixture (Hoydonckx et al., 2007; Montastruc et al., 2011). Xylitol yield could reach a maximum of 0.7 g/g and production rate can be of 0.46 g xylitol/h L (Fatehi et al., 2014). Purified fermentation broth concentrated to 400 g xylitol/L achieved 68% yield and 99% purity after crystallization (Misra et al., 2011).

Mass balance and energy consumption for the three scenarios are summarized in Table 2 (values per ton of bagasse).

Scenario 1 produces 514 kg of xylose syrup, 382.1 of gypsum salt and 167 kg of adsorbed compounds (mainly phenolic compounds, acetic acid, furfural, HMF, and extractives), as shown in Fig. 2. Total water removed by evaporation is 6200.9 kg. Autohydrolysis and evaporation processes demand 95.5% of the consumed energy. Scenario 2 produces 139.2 kg of furfural and the energy demand is similar to the energy consumed for the production of xylose syrup. Water removed is 6368 kg, similar to Scenario 1. In Scenario 3, products are 106 kg of gypsum salt, 160.6 kg of adsorbed compounds, 93.9 kg of xylitol, and 167 kg of adsorbed compounds (mainly phenolic compounds, acetic acid, furfural, HMF, extractives and residual nutrients of fermentation broth).

Total water removed by evaporation is 6200.9 kg. Autohydrolysis and evaporation processes demand 97% of consumed energy. Total water removed by evaporation is 5915 kg. The energy consumed for xylitol production is 18% and 23% greater than for xylose syrup and furfural, respectively. The amount of consumed water is the same in the three hypothetical scenarios.

Table 2 shows the energy requirements for the main processes. Autohydrolysis treatment and evaporations are energy intensive operations because of the high temperature and the large amounts of water involved. In the post-hydrolysis processes of Scenarios 1 and 3, H_2SO_4 used is 3% w/v, whilst it is 4% w/v in Scenario 2. The residual solid generated by the autohydrolysis leaves the process with 100% of moisture, and is sent to produce energy or MDF fiber boards.

In Scenario 3, the evaporation and adsorption processes remove inhibitor compounds for fermentation. Volatile compounds such as acetic acid and furfural are removed together by evaporation with the steam stream and they remain in the condensed water. Condensed water could be sent to a wastewater treatment plant (not considered in this study). The details of all evaporator effects for each scenario are listed in Table 3. We suppose that 70% of nutrients are used in the fermentation broth are consumed by the yeast and the remaining 30% must be removed by activated carbon adsorption.

3.3. Economic analysis

3.3.1. Capital cost investment

An economic assessment for the installation and production of the three scenarios from hemicellulose bagasse conversion was performed. The direct and indirect costs of the installations were estimated according to the modified National Renewable Energy Laboratory method (NREL) (Pham et al., 2012). As first step in the economic analysis, the equipment costs were estimated considering the installation and scaling factors (Humbird et al., 2011; Pham et al., 2012; Couper et al., 2004; Peters and Timmerhaus, 1991; Treasure et al., 2012; Sinnot, 2013; Silla, 2003; Mercado libre, 2015; Matche, 2015; Alibaba, 2015). These costs were estimated for a capacity of 15,000 t/year of dry bagasse. A

	Ea (kJ/mol)	Ea (°K)	ln(k_0)
k_h	142.7	17,177	39.7
k_1	158.1	19,028	41.7

Table 1 – Arrhenius' parameters and kinetic constants determined for the autohydrolysis process.

k_{0i}, preexponential factors, E_{ai}, activation energies, $R = 8.31 \times 10^{-3}$ kJ mol^{-1} °K^{-1}.

Table 2 – Mass balance (kg per ton of dried bagasse) and energy consumption (MW per ton of dried bagasse).

	In solid (kg t^{-1})	In liquid (kg t^{-1})	Out solid (kg t^{-1})	Out liquid (kg t^{-1})	Energy (kW t^{-1})
Scenario I. Xylose syrup production					
Autohydrolysis	1000.0	7000.0	816.0	816.0	1541.2
Poshydrolysis[a]		6367.9	382.1		147.1
Adsorption1		6367.9	167.0		36.8
Evaporation		6200.9		5687.0	2400.3
Total product				514.0	
Total energy					4125.3
Scenario II. Furfural production					
Autohydrolysis	1000.0	7000.0	816.0	816.0	1541.2
Acid Hydrolysis		6368.0			693.3
Purification[b]		6368.0		6228.8	1595.7
Total product				139.2	
Total energy					3830.2
Scenario III. Xylitol production					
Autohydrolysis	1000.0	7000.0	816.0	816.0	1541.2
Evaporation1		6368.0		4589.4	1911.3
Poshydrolysis[a]		1778.6	106.7		124.1
Adsorption1		1778.6	156.0		12.2
Fermentation		1622.6	132.3		124.6
Adsorption 2		1490.3	4.6		6.1
Evaporation 2		1485.7		1188.7	1000.7
Crystallization		297.0		203.1	245.7
Total product			93.9		
Total energy					4965.9

[a] Correspond to post-hydrolysis and neutralization with Ca(OH)$_2$.
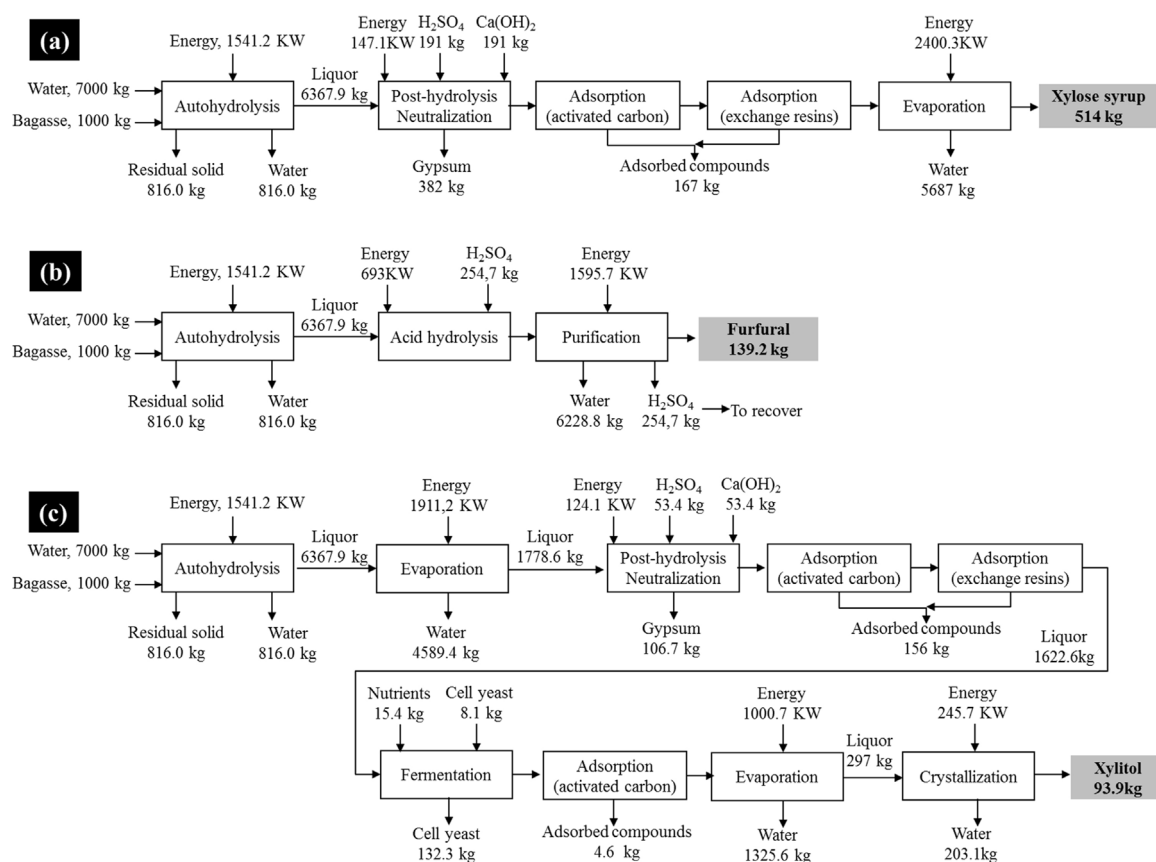[b] Correspond to distillation process.

Fig. 2 – Principal inlet, outlet and internal streams of the processes (a) Scenario 1. Xylose syrup, (b) Scenario 2. Furfural, and (c) Scenario 3. Xylitol.

construction period of 1.5 years is assumed for the biorefinery. We assume that operation starts at 50% of the mill capacity in the second year, and it operates at full capacity in the rest of the life time (10 years). Methods to estimate the Total Costs Investment (TCI) are summarized in Table 4. TCI is 3.5 times greater than the purchased equipment costs using the modified NREL method. Unit prices for bagasse, chemicals, products, energy, labor, and maintenance are showed in Table 5.

Table 3 – Details of evaporators for concentration of liquid streams.

Area m^2	Temperature (°C)	EPE (°C)	Pressure (bar)	Energy (kW)
Scenario 1—evaporation (3-effects)				
27.7	98.9	0.08	0.96	909.5
22.6	77.4	0.16	0.42	741.7
22.8	56.4	1.71	0.16	749.1
Scenario 3—evaporation 1 (3-effects)				
21.7	97.9	0.07	0.95	745.0
16.9	75.4	0.11	0.40	580.2
17.1	53.5	0.24	0.14	586.0
Scenario 3—evaporation 2 (3-effects)				
24.7	53.0	0.56	0.14	311.8
24.7	43.4	0.72	0.09	333.6
21.2	28.7	5.56	0.04	355.3

Table 4 – Total Costs Investment (TCI) for all scenarios.

Cost Items	Factor	Scenario costs (USD) for 15,000 t bagasse/year		
Total direct costs				
Purchased equipment	1.000	1018,084	1497,976	7864,537
Installation[*]	~0.700	884,617	1497,087	6929,102
Warehouse	0.025	25,452	37,449	196,613
Site development	0.153	155,767	229,190	1203,274
Total indirect costs				
Prorateable costs	0.188	191,400	281,620	1478,533
Fixed expenses	0.188	191,400	281,620	1478,533
Office and construction	0.470	478,500	704,049	3696,332
Contingency	0.282	287,100	422,429	2217,799
Other	0.188	191,400	281,620	1478,533
FCI (fixed capital investment)	3.194	3423,719	4784,537	25,119,330
Working capital investment (WCI = 10% of FCI)	0.320	325,176	4784,537	2511,933
Total Costs Investment (TCI)	**~3.520**	3748,896	5711,494	29,055,190

[*] This factor varies for each type of equipment. TCI calculation is based on an average value of Installation cost of 0.7.

3.3.2. MDF boards production from bagasse

Eq. (5) is used to estimate the capital required for a project based on biomass production at different scales (Silla, 2003; Sadhukhan et al., 2014; Wright and Brown, 2007).

$$C = Co \left(\frac{M}{Mo} \right)^n \tag{5}$$

Table 5 – Unit prices for bagasse, chemicals, products, energy, labor, and maintenance.

Unit prices at mill gate	
Bagasse (USD/t)	7.018[a]
Water (USD/m^3)	0.585[b]
Electricity (USD/MW)	51.46[c]
Labor (USD/h)[*]	3.09–4.41(assumption)
Maintenance and taxes	8% (of revenue)
Chemicals for production [d]	
H_2SO_4 (USD/kg)	0.039
$Ca(OH)_2$ (USD/kg)	0.134
Fermentation (USD/kg)[**]	0.112
Products (assumptions)	
Xylitol (USD/kg)	8.5
Xylose Syrup (USD/kg)	0.6
Furfural (USD/kg)	1.5

[*] Value depends of the worker position.
[**] Nutrition, yeast, etc.
[a] Price estimated from the Instituto Nacional de Tecnología Agroindustrial (INTA, 2013).
[b] Average Price in Argentina (Tarifas de Agua Potable, 2015).
[c] Energy Cost in Misiones, Argentina (EMSA, 2015).
[d] Treasure et al., 2012.

where C is the investment cost of a plant with a capacity M, Co is the investment cost of the reference plant with a capacity Mo, and n is an exponent less than one (Wright and Brown, 2007). Reference values to estimate production capacity and capital investment were taken from (Taupier and Bugallo, 2000; ATCP Chile, 2008). Energy consumptions were estimated with the results presented by Li and Pang (2006). Table 6 shows the investment, capacity and energy consumption for MDF fiber board production (MDF prices: 300–400 USD/m^3, (Alibaba, 2015; Taupier and Bugallo, 2000)).

Table 7

Table 6 – Investment, capacity and energy consumption for MDF fiber board production.

Details	
Investment USD	18,025,468.5
Capacity per year (m^3)	13,249.9
Capacity per hour (m^3)	1.93
Price adopted (USD/m^3)	320
Energy consumption (MW h)	2.60

Table 7 – Investment, capacity and yield for energy generation.

Details	
Investment (USD)	3,068,699.1
Capacity per year (MW)	18,636.3
Yield	0.72
Capacity per hour (MW h)	2.70

Table 8 – Comparative results for different the three studied scenarios of biorefinery from the economic analysis.		
Residual solid conversion	Total capital investment (USD)	IRR (%, 5 years)[*]
Scenario I. Xylose syrup		
Energy generation	6,492,927.4	12
MDF	21,449,696.8	19
Scenario II. Furfural		
Energy generation	8,302,488.1	1
MDF	23,259,257.5	16
Scenario III. Xylitol		
Energy generation	29,615,887.8	10
MDF	44,572,657.2	8

[*] Since the mill started to produce. IRR of each scenario was calculated taking into account two alternatives to the conversion of residual solid (energy generation or MDF).

3.3.3. Energy generation

As another alternative use of the dried residual solid, the investment cost for an electric generation plant was estimated. The residual solid produced per year is about 12,200 t, so this value was used to estimate the total energy that could be produced. The total investment costs were estimated by Humbird et al. (2011) and Nussbaumer and Oser (2004).

3.3.4. Economic evaluation

The internal rate of return (IRR) is a tool for evaluating and ranking projects widely used in practice (Weber, 2014). High IRR generally indicates that the project is economically attractive. For this study it is considered that a project is economically viable when the IRR (for a period of 5 years) is greater than 15%. Results are shown in Table 8. Despite the lower prices of xylose syrup and furfural regarding xylitol price, the IRR values showed that the best investments options are the production of xylose syrup and furfural combined with MDF fiber board production. This can be attributed to the low investment costs of these scenarios. Xylitol is a high value added product in the market and its high investment cost result in a less attractive IRR (for the considered period and production volume), but processes such as fermentation, crystallization, etc., must be optimized. Although xylitol production from a new plant appears unattractive, it would be interesting to analyze the feasibility of integrating its production to an established production chain (e.g., sugar mill), that could significantly reduce the investment costs.

4. Conclusions

The study analyzed the possibility to integrate the production of tree different products from hemicellulose with an alternative utilization of the residual lignocellulosic material to produce MDF fiber board or of energy generation. The problem was considered from both the technical and economical points of view. The IRR values for different scenarios showed that the Scenario I with MDF fiber board production is the most profitable alternative due to lower capital investment. The better second alternative is furfural with MDF fiber board production (lower IRR). In the case of xylitol production, the IRR is relatively low due to the high investment cost (despite of the high price of this product). Process optimization and performance enhancement of the operations as autohydrolysis, fermentation and crystallization would improve its

profitability. These alternatives could contribute significantly to the total revenues of sugar mills by the integration of small plants to produce high value added products from sugarcane bagasse, like it is demonstrated in this study.

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