

Alternatives of Small-Scale Biorefineries for the Integrated Production of Xylitol from Sugarcane Bagasse

Nicolás M. Clauser^{1*}, Soledad Gutiérrez², María C. Area¹, Fernando E. Felissia¹ and María E. Vallejos¹

¹Materials Institute of Misiones (IMAM), National University of Misiones – National Council of Scientific and Technical Research (UNaM – CONICET), 1552 Félix de Azara St. (3300), Posadas, Misiones, Argentina

²Faculty of Engineering, University of the Republic (UDELaR), 565 Julio Herrera y Reissig St. (11700), Montevideo, Uruguay

Received December 31, 2016; Accepted May 2, 2017

ABSTRACT: Small-scale biorefinery from sugarcane bagasse offers new possibilities to the sugar and ethanol industries. The aim of this study was to evaluate the feasibility of a small-scale biorefinery for the production of xylitol from sugarcane bagasse. The liquid fraction from the autohydrolysis treatment was selected as the source of sugars for xylitol and two scenarios were analyzed for the residual solid: ethanol or pellet production. A technical-economic analysis of alternatives was applied. The internal rate of return (IRR) was used to compare the selected proposals. The highest IRR values were obtained when processing 70,000 dry tons per year of bagasse. The results showed promising prospects for a small-scale biorefinery with capacities above 20,000 dry tons per year (xylitol and pellets), and above 50,000 dry tons per year (xylitol and ethanol).

KEYWORDS: Biorefinery, sugarcane bagasse, xylitol, ethanol, pellets

1 INTRODUCTION

Bioproducts and biofuels have gained increasing interest during the last years, as they are a means to decrease greenhouse gas emissions and a solution to reduce oil dependency. Lignocellulosic biomass (corn stover, sugarcane bagasse, wood, and others) are potential feedstocks for the production of fuels and chemicals in biorefineries. However, these materials have a complex polymeric structure composed mainly of cellulose, hemicelluloses and lignin, which requires a previous fractionation to allow their conversion to high-value products.

The most typical biorefinery scenario is based on the extraction of sugars from biomass to produce cellulosic ethanol, steam and electricity. This classic scheme needs to be improved to achieve a more efficient use of both lignocellulosic feedstocks and energy. The development of a systematic methodology to combine a large number of lignocellulosic feedstock, product, and process configurations in an integrated biorefinery is a great challenge. The conversion of lignocellulosic feedstock to products is complex and depends on several factors, including the feedstock type, the price

of energy and products, the production scale, and the required conversion technologies. The production processes can be designed in different scales (micro, small, medium and large), and for each process it is possible to determine the optimal scale to increase profitability using an optimization and integration procedure. There are different ways of classifying the scales of industries. These scales can be classified taking into account factors such as the number of workers (less than 50 for small scale), annual sales, production volumes, the relationship between these factors, and others.

Some advantages of small-scale biorefineries are lower capital and logistics costs, and lower inversion risk than those of large-scale ones, in addition to the possibility of labor occupation in rural areas [1]. Biorefineries should obtain as much value as possible from lignocellulosic materials through the optimal selection of products. High-value specialty products are prized above commodities (e.g., biofuels up to USD 1.0 per liter). Viable strategies can combine the production of low-value commodities at large scale with the production of high-value products at small scale. Sugarcane has a strategic role in the energy matrix and the economy of the main developing countries (Brazil, India and China), producing three large-scale products: sugar, ethanol, and electricity. Brazilian sugarcane harvest was estimated

*Corresponding author: nicolas.clauser@gmail.com

at approximately 654.6 million tons in 2015–2016 [2] with more than 448 first generation ethanol mills from this raw material [3]. In Argentina, sugarcane production is one of the most important agro-industrial crops, being around 20.5 million tons in 2013, and it is expected that this production will grow 10% in 2016 and 33% in 2020 [4]. Sugar and ethanol mills generate about 280 kg of bagasse (50% humidity) per ton of processed sugarcane.

Sugarcane bagasse is composed of 43% cellulose, 21–23% lignin, 25–32% hemicelluloses (mainly xylans), minor amounts of soluble organic compounds, and inorganic compounds (the percentages are based on the dry weight of bagasse) [5]. Hemicelluloses from sugarcane bagasse are mainly composed of xylans, which can be hydrolyzed to oligomers and sugars. Xylose is the cheapest pentose and one of its main derivative products is xylitol. Xylitol is used as food sweetener and moisture-retaining agent in pharmaceutical and cosmetic products. Xylitol production is expanding on a global scale [6], with a strong total demand of more than 125,000 tons per year [7] and its overall consumption is expected to reach 242 thousand tons by 2020, equivalent to USD 1,000 million [8]. Depending on the final product (pharmacies, supermarkets, etc.), prices are about USD 5–20 kg⁻¹ [6, 7].

Complementary to first-generation ethanol production, sugarcane bagasse can be used to produce second-generation ethanol by acid or enzymatic hydrolysis of cellulose.

It is predicted that the growth in the production of fuels will not match the projected demand rate for 2040–2050, since the level of oil demand will increase from 85 million barrels d⁻¹ in 2008 to 105 million barrels d⁻¹ in 2030, and higher thereafter [9]. Bioethanol is considered the most promising biofuel from renewable resources and efforts have increased in its commercial production in recent years. The development of second-generation bioethanol made from lignocellulosic biomass can increase the sustainability of feedstock production competing with neither food production nor with farmland.

So far, sugarcane bagasse is the most efficient lignocellulosic material for bioethanol production, involving four major unit operations: pretreatment to remove lignin and/or hemicelluloses, hydrolysis of polysaccharides to sugars, fermentation of sugars into ethanol, and ethanol recovery. Acid hydrolysis is usually performed at high temperature using diluted H₂SO₄. Even though the process is slower, enzymatic hydrolysis has shown better results because acid hydrolysis generates inhibitory compounds for ethanol fermentation from glucose [10]. Another disadvantage is that problems related to corrosion of the equipment may occur due to the use of acids (even in low concentration),

requiring expensive materials for the construction of the reactors, which increases the costs [11, 12]. Also, the hydrolysate has a low pH and needs to be neutralized before being used as fermentation medium. Formation of compounds toxic for microorganisms may also occur during the process. Since the concentration of sugars in the hydrolysate is usually low an additional step of concentration is required before its use as fermentation medium [12]. Enzymatic hydrolysis can be carried out separately from the fermentation (separate hydrolysis and fermentation, SHF) or both processes can run together (simultaneous saccharification and fermentation, SSF) [10]. The advantage of SHF is that the processes can be carried out at their optimal conditions, since the optimum temperatures for enzymatic hydrolysis and alcoholic fermentation are about 45–50 and 28–35 °C, respectively. On the contrary, this does not happen in the SSF configuration [13]. However, the SSF process has shown great advantages over SHF in terms of capital cost (about 20% reduction of the investment cost), operation time, and processing complexity [3]. Another advantage of SSF is the reduction of the inhibitory effect on the enzymes of the hydrolyzed glucose [14]. Ethanol also inhibits hydrolysis but to a lesser extent than cellobiose or glucose [15].

Nowadays, the SSF uses very expensive inputs with moderate yields, which do not make it suitable for large-scale use [16]. The success of second-generation production depends on the government policies because the capital investment in this route is undeniably high and risky. Policies will not only help uplift the possibility of second-generation production but they will also allow the suppression of environmental harm caused by the emissions of the non-renewable energy products [17]. However, there is little information available about the SSF process to obtain ethanol from sugarcane bagasse treated by autohydrolysis and alkaline delignification. The characteristics of the residual solid obtained by steam explosion, diluted acid, and autohydrolysis treatments can be considered comparable [3]. The main difference between these treatments is the severity of the operating conditions.

Pellet production is an interesting option for industries that have significant volumes of lignocellulosic waste. This waste should be sourced locally because its low bulk density makes it costly to transport over long distances [18]. Pellets are an environmentally friendly alternative to reduce fossil fuel dependency and one of the renewable forms of energy that can contribute to achieving the goals of international agreements with regard to the production and use of renewable energy sources [19]. Their price varies between 120 and 156 USD per ton [20]. The advantages of pellets as solid fuel are their characteristics of easy transportation

(due to their shape and size) and homogeneous quality. Densification can partly solve the logistical problems associated with large volumes of biomass, but the low strength and moisture sensitivity of pellets make their storage and transportation over long distances difficult [21]. Therefore, the benefit of pretreating the solid to improve the quality of this material has been established. Studies on pretreatment of *Salix* with SO₂ steam explosion determined that there is a remarkable improvement in the mechanical strength, moisture resistance and density of pellets, besides an improvement of their heat capacity and low ash content [22].

Economic studies are key in the biorefinery analysis to allow the commercial implementation of the manufacture of products derived from biomass, their financial viability and financial support during their development. Economic engineering tools are used to assess the required investment, profitability (internal rate of return [IRR], net present value [NPV] and other parameters), revenues, production costs, minimum selling prices of products, and taxes in the production processes. The implementation of new technologies requires sensitivity analysis of the technical parameters on the related costs and investments, and related risk analysis.

The aim of this study was to evaluate the feasibility of a small-scale biorefinery for the production of xylitol from the liquid fraction of sugarcane bagasse autohydrolysis, combined with the production of ethanol or pellets from the residual solid. A model for a small-sized biorefinery was developed, determining the best scenario based on market prices of the products, production costs, and IRR estimation for the selected scenario.

2 METHODS

2.1 Raw Material

The study was based on sugarcane bagasse from a local mill (San Javier Sugar Mill, Misiones, Argentina). Detailed methods of bagasse depithing, chemical composition determination, and results can be found in a previous study [23].

2.2 Xylitol Production

The processes involved in the conversion of the hemicellulosic liquor to xylitol and the production of two alternative products from the residual solid (ethanol or pellets) are shown in Figure 1.

The proposed method to produce xylitol involved autohydrolysis of bagasse, concentration of liquid fraction, acid post-hydrolysis, removal of inhibitors by adsorption, fermentation of xylose to xylitol, and

xylitol recovery by crystallization. The xylose extraction from bagasse occurs through a hydrolysis reaction autocatalyzed by acetic acid. The fermentation of xylose to xylitol is produced by a biological reduction reaction through microorganisms.

In the autohydrolysis treatment, a liquid-to-solid ratio (LSR) of 5.5:1 is used as it is usual at industrial scale and the energy demand in the evaporation stage is acceptable [24], since in a previous work [25] we found that a liquid-solid ratio of 7:1 was significantly higher, requiring excessive investment and production costs. The optimum temperature and time to maximize xylans extraction, minimizing the energy requirements, were estimated from the model developed by Clauser *et al.* [25]. The model describes the autohydrolysis process for different treatment conditions, and was applied to optimize the autohydrolysis when the liquid-solid ratio is reduced from 7:1 to 5.5:1. GAMS software (CONOPT solver) was used.

A falling film evaporator was selected to concentrate the liquid fraction. Acid post-hydrolysis was used (3% of H₂SO₄, at 120 °C for 60 min) to convert xylo-oligomers to xylose (100 g L⁻¹ of xylose). The addition of Ca(OH)₂ in a stirred tank was utilized to neutralize the acid. Gypsum salt is separated by filtration (>90%). Detoxification of liquid fraction with about 100 g L⁻¹ of xylose is accomplished in two stages: (1) adsorption with activated carbon columns to remove HMF, furfural and 90% of phenolic compounds; (2) adsorption with ion exchange columns (adsorptive, a strong base anion and weak acid cationic exchange resins) to remove residual phenolic compounds, acetic and formic acids, and harmful cations. Details about all stages can be found in a previous work [25].

Fermentation conditions of the detoxified liquid fraction (100 g L⁻¹ of xylose) were selected from Ping *et al.* [26]. The detoxified stream is fermented to xylitol by *Candida tropicalis* with a productivity of 0.46 g xylitol h⁻¹ L⁻¹ and a maximum yield of 0.7 g_(xylitol) g_(xylose)⁻¹. Cell yeast is separated by membrane filtration, and nutrients and other impurities in the fermentation broth are removed by activated charcoal columns (color and odor removal) [27]. The scheme ends with the concentration of the liquid stream by falling film evaporators and crystallization in 4 cycles.

2.3 Scenarios for the Valorization of the Residual Solid

Complementary to xylitol production from xylans of the hemicellulose fraction, two scenarios were assessed as strategies to exploit the residual solid from sugarcane bagasse autohydrolysis.

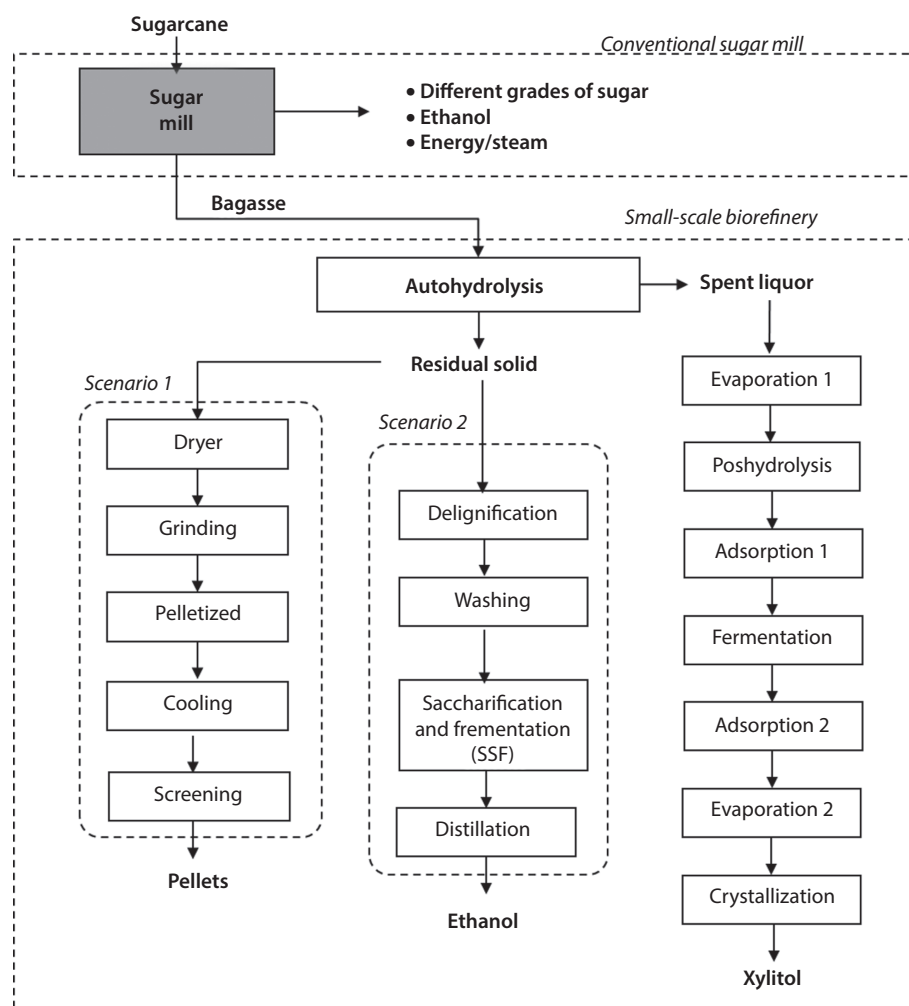


Figure 1 Simplified block flow diagram for the processes involved in the three studied scenarios.

2.3.1 Scenario 1 – Ethanol Production

Enzymatic hydrolysis of lignocellulosic material generally depends on the initial composition of the material, the employed pretreatment methods, and the enzymes used for saccharification of cellulose to glucose.

Alkaline delignification increases the internal surface of cellulose, decreases the degree of polymerization and crystallinity and disrupts the lignin structure [10]. Organosolv delignification (alkaline or acid) is conducted at higher temperatures than soda process [28]. This means an important increase of energy consumption and the need for stringent safety conditions. Hot water pretreatment followed by alkaline delignification have shown cellulose conversion to ethanol (around 90%) similar to steam explosion treatment followed by alkaline delignification [29]. Alkaline delignification was then selected for lignin removal after the autohydrolysis treatment to increase enzymatic hydrolysis yield because of its efficiency and low cost

[30, 31]. The alkaline delignification is based on three groups of reactions: fragmentation, degradation and dissolution, and condensation of lignin, hydroxyl ions being responsible for delignification [32].

In this scheme, residual solid from autohydrolysis is fed into the digester and it is delignified with NaOH. Subsequently, delignified solid is crosscurrent washed in vacuum filters usually used in the pulp and paper industry. Washing water containing lignin, other dissolved organic solids, and NaOH, are concentrated in evaporators together with black liquor. In the case of integrated biorefineries at the sugar mill or in the paper industry, this concentrated stream can be burned in a recovery boiler to produce power or process steam. An example of this alternative is Ledesma S.A.A.I. (Argentina) which processes more than 3.5 million tons of sugarcane annually (2014) to produce sugar, ethanol, and cellulosic pulp and paper. Another alternative is the recovery of lignin by precipitation at pH < 3, which is the least

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

attractive because the market and price of lignin is difficult to predict. The conditions adopted in the present study (Table 1) for the delignification process were proposed by Soares and Gouveia [30], who used a solution of NaOH at 1% w/v (about 10% NaOH based on the dry weight of bagasse). A liquid-to-solid ratio of 4:1 was adopted, since it is usual in the pulp industry [33].

Subsequently, the cellulosic fraction of the delignified solid is enzymatically hydrolyzed to glucose and fermented to ethanol by a simultaneous saccharification and fermentation (SSF) [10]. The SSF process conditions were selected from the updated literature [30] involving a solid-to-liquid ratio of 9:1 (w/v) for 48 hours. Enzymes and nutrients are first added at 50 °C to hydrolyze cellulose for 6 hours, and then yeast and nutrients are added after cooling to 37 °C. The ethanol is recovered by a conventional separation sequence, which consists of two distillation columns. Finally, molecular sieve columns are used downstream to obtain anhydrous ethanol.

2.3.2 Scenario 2 – Pellet Production

Pellet production from the residual solid of the autohydrolysis treatment of sugarcane bagasse could be

an interesting option. The selected processes for pellet production, based on the updated literature [18, 34], involve drying, grinding to reduce the particle size, pelletizing, cooling to allow solidifying and strengthening of the pellets to provide strength and durability to granules, and finally screening through a vibrating sieve to remove fine material and ensure a clean fuel source. The fine material is recovered by introducing it back into the pelleting process. After screening, pellets are ready to be packaged.

The calorific value of the bagasse before and after the autohydrolysis treatment are compared by the higher heating value (HHV) parameter, as shown in Equation 1 [35]:

$$HHV \text{ (MJ kg}^{-1}\text{)} = 0.1736C_e + 0.2663L + 0.3219E \quad (1)$$

where C_e , L , E are the weight percent on dry biomass basis of polysaccharides (cellulose and hemicelluloses), lignin, and extractives, respectively.

The main operation parameters of the conversion processes used to evaluate the feasibility of a small-scale biorefinery for the production of xylitol combined with the alternative production of ethanol or pellets are shown in Table 1.

Table 1 Main operation parameters of the conversion processes.

Stage	Process conditions	Scaling factors
Xylitol production		
Autohydrolysis (Reactor)	162 °C; 2 h; LSR: 5.5 [24, 25]	0.78 [39]
Evaporation	To reach 100 g/L of xylose [25]	0.54 [36]
Poshydrolysis (Reactor)	120 °C; 1 h; 3% H ₂ SO ₄ [28]	0.78 [39]
Adsorption	Activated charcoal (32g/L) and exchange resin [25]	0.7 [37]
Fermentation	35 °C; pH 5–7; 40 h [26]	0.67 [39]
Adsorption	Activated charcoal (20 g/L) [43]	0.7 [37]
Evaporation	To reach 400 g/L of xylitol [25]	0.54 [36]
Crystallization	From –20 °C to 8 °C in 4 cycles [43]	0.37 [36]
Ethanol production		
Delignification (Reactor)	100 °C; 30 min; 2% NaOH; LSR: 4 [30, 33]	0.78 [39]
SSF (Reactor)	From 50 °C to 37 °C, during 48 h [30]	0.67 [39]
Recovery	Two columns at 2 bar to reach 91 ~ 92% w/w ethanol. Molecular sieve columns to reach 99.8% w/w ethanol [44]	0.7 [39]
Pellets production		
Drying	Rotary drier with hot air to reach 12–17% moisture [18]	0.6 [21]
Grinding	Hammer mill, particle size reduction to < 6 mm [18]	0.6 [21]
Pelletized	High pressure pelletizer (~1 t/h), 8–5% final moisture [18]	0.85 [21]
Cooling	Countercurrent air (~20 min) [18]	0.58 [21]
Screening	To remove and recover fine material [18]	0.6 [21]

2.4 Mass and Energy Balances

To accomplish the mass and energy balances the main flows involved in each step of the different processes formerly described were considered. Yields of the different operations and reactions, nutrients and microorganisms, chemical reagents, supplies, etc., were established on the basis of an updated bibliography. The energy balance was developed by calculating the energy consumption of equipment and processes, and the need for heating and cooling of the different streams. For utilities, electricity consumption of the process and related equipment, and water heating and cooling were estimated as proposed by Stuart and El-Halwagi [36]. Apache OpenOffice Calc 4.1.1 software was used for the mass and energy balances.

2.5 Economic Analysis

“Small scale” is a relative concept, which should be defined in any case. In cases where there is availability or logistical restrictions on the raw material, a potential strategy is to treat it locally to produce high added-value products. This strategy is even more effective if the valuable product obtained can be consumed locally, to reduce the transport cost. Therefore, small-scale biorefinery is defined by low consumption of raw materials and low volumes of high added-value products. This was the criterion adopted in this study.

The economic analysis was performed considering the process design and estimating the production costs, labor costs, and capital investment, among others [36–38].

Equation 2 is used to estimate the capital required for the project based on biomass production at different scales:

$$C = C_o \left(\frac{M}{M_o} \right)^n \quad (2)$$

where C is the process equipment cost of a plant with a capacity M , C_o is the reference cost of a plant with a capacity M_o , and n is an exponent smaller than one. Different scaling factors, cost installations, and other costs were estimated from the updated literature [36–38].

Labor requirements were calculated based on the type of process (batch process) and the capacity of the facility [39].

The availability of raw materials was established as 15,000 tons per year of dry bagasse. The internal rate of return (IRR) is used as an indicator of the profitability of potential investments of biorefinery projects [3, 36]. IRR was selected as a reliable measure for a first estimation [37]. The higher the IRR, the higher is the profitability of potential investment. To

determine the biorefinery scale based on IRR values, the technical and economic analysis of each proposed scheme was evaluated considering different annual volumes of processed raw material. These proposed scenarios were analyzed with Apache OpenOffice Calc 4.1.1 software [40] and cash flows were also determined.

3 RESULTS AND DISCUSSION

3.1 Raw Material

The chemical composition of raw material (as a percentage of oven-dry weight of 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 [23].

3.2 Xylitol Production

Optimal temperature and time estimated with a liquid-to-solid ratio of 5.5:1 to maximize xylose solubilization were 162 °C and 120 minutes. The highest amount of xylans (oligomers + xylose) that can be obtained in the liquid fraction of sugarcane bagasse autohydrolysis at optimal conditions is 18.3% by weight (77 wt% of initial xylans content in bagasse). These results of temperature, time, and yield are similar to those obtained in a previous study [25]. After the pretreatment, the spent liquor is concentrated in a falling film evaporator system before the post-hydrolysis [27, 41] and then it is detoxified by adsorption columns. Then the fermentation is performed (temperature, nutrient concentrations, aeration, and pH) under conditions selected from Ping *et al.* [26]. *Candida tropicalis* yeast is the inoculum to ferment the xylose to xylitol. Inoculum is prepared in a stirred batch fermenter and afterwards transferred to a larger fermenter at 5 g cell yeast/L. The fermentation of xylose is performed at 35 °C and pH 5–7 for 40 h [26]. After fermentation, it is necessary to remove cell yeast, nutrients, and other impurities from the fermentation broth using membranes filtration and activated charcoal columns. Finally, concentration (using falling film evaporators) and crystallization were applied. The crystallization of xylitol occurs at temperatures less than –10 °C, since above this temperature no crystallization occurs.

Input streams for xylitol production are water, chemicals (H_2SO_4 , $Ca(OH)_2$), yeast, and nutrients. Products and by-products (expressed per dry ton of bagasse) are 93.9 kg of xylitol, 106 kg of gypsum salt and absorbed compounds (20 kg of acetic acid, 6 kg of furfural, 8 kg of extractives, and 2 kg of formic acid). About 120 kg of activated carbon and exchange

resins are used. After the fermentation stage, only 5 kg of residual nutrients of the fermentation broth are adsorbed.

Mass balance and energy consumption for the whole scheme are summarized in Figure 2 (values expressed per ton of bagasse).

Total water removed by evaporation is 4,278 kg. Condensed water could be recycled to different washing stages.

Gypsum, recovered in a set of filter presses, is a low-value by-product (USD 8 per ton), which can be sold to farmers as fertilizer and soil conditioner [27, 42]. The post-hydrolysis yield to convert xylo-oligomers to xylose was estimated to be 94% [23]. In the fermentation stage, the xylose stream coming from the detoxification stage is fermented to xylitol by *Candida tropicalis*. Purified fermentation broth concentrated to 400 g xylitol L⁻¹ achieved 68% yield and 99% purity after crystallization [43].

The energy consumption in autohydrolysis and liquor concentration by evaporation were 1,281 and 1,367 kW, respectively. This means a reduction of 16 and 28% in energy consumption in each process respectively, with respect to the energy consumption in the same process but using a liquid-solid ratio of 7:1 [25]. In addition, considering both processes, working with a liquid-solid ratio of 5.5:1 would mean a reduction in energy consumption of 23% (compared to energy consumption when using a liquid-solid ratio of 7:1) [25]. Another advantage is that small equipment can be used and higher concentration of products can be obtained.

Details of evaporator effects of the concentration of autohydrolysis liquid fraction for xylitol production are listed in Table 2.

The energy consumed for xylitol production is 4,162 kW. It represents 67% and 88% of total energy consumed for xylitol + ethanol and xylitol + pellet production respectively.

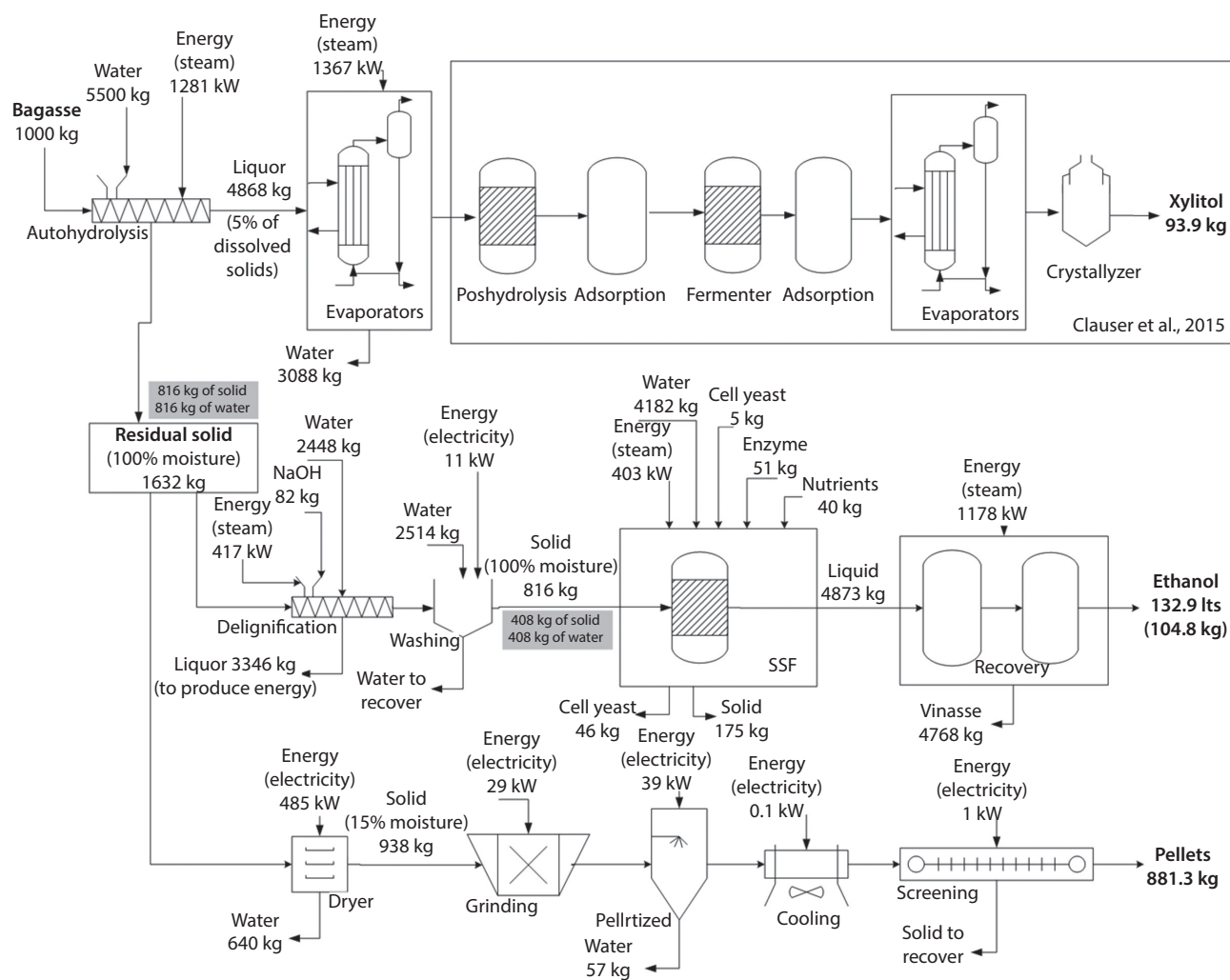


Figure 2 Principal inputs, outputs, and internal streams of the processes in the different studied scenarios.

Table 2 Details of evaporators for concentration of liquid streams.

Evaporator (3 effects)				
Area (m ²)	Temperature (°C)	BPE (°C)	Pressure (bar)	Energy (kW)
15.8	97.9	0.09	0.95	540.3
12.0	75.4	0.13	0.40	411.3
12.1	53.5	0.24	0.14	415.4

BPE: Boiling-point elevation

3.3 Scenarios for the Valorization of the Residual Solid

3.3.1 Ethanol Production

The delignification and SSF treatments of the residual solid from autohydrolysis demand high water consumption (delignification, washing of cellulose fibers and SSF). Other input streams are chemicals (NaOH), enzymes, yeast, and nutrients. In delignification, a liquid-solid ratio of 4:1 and 2.5% (w/v) NaOH are used to obtain 50% (w/w) of yield, which represents 81.6 kg of NaOH per 816 kg of pretreated sugarcane bagasse. Assuming 90% of delignification yield, 408 kg of cellulosic fibers are obtained. The liquor stream of 3,346 kg, with around 216 kg of lignin, could be burned to generate 2,108 kWh.

Enzyme charge for SSF process was 10 FPU g⁻¹ of cellulose, and fermentation was performed with an initial yeast cell concentration of 1 g L⁻¹ (Figure 2). Conversion of cellulosic fibers to ethanol by SSF is around 72% of the potential ethanol that could be obtained from cellulose (theoretical yield of 0.568 g of ethanol per g of cellulose). Ethanol production is around 133 L (or 105 kg) per ton of dry bagasse after the purification. Considering a purification yield of about 91%, 4,768 L of vinasse are removed.

In the conversion of residual solid to ethanol, delignification, SSF, and ethanol recovery/purification consume 2,008 kW per ton of dry pretreated bagasse. Delignification and recovery are the greatest energy consumption stages, as about 79% of the energy used in ethanol production is consumed in these stages. In the scenario “xylitol + ethanol,” the energy consumed by delignification, SSF, and recovery represents 33% of the total energy in this scenario.

3.3.2 Pellet Production

Pellet production is technologically simpler than the other two processes (xylitol and ethanol production). Conditions for pellet production were selected from references [18, 20, 34]. Pellet production can be

0.73 m³ per ton of dry bagasse (881 kg per ton of dry bagasse considering a density of 1,200 kg m⁻³). In the drying process, final moisture content has to be about 15%, so 694 kg of water by ton residual solid must be removed in this step. An adequate grinding of raw material results in a high degree of compaction of pellets and fines reduction [34]. In pelletizing, 57 kg of water are removed from the material because the mechanical treatment can increase the temperature to 100 °C due to friction, allowing 5–8% of moisture content in pellets. Pellets are subsequently air cooled to solidify lignin, strengthening the pellets. In contrast to the drying process, cooling does not involve any additional energy [18]. Finally, in the screening process, the “fines” recovered are returned to the pelletizing process to ensure that no raw material is wasted. The drying process consumes 485.4 kW, representing about 88% of the total energy used for pellet production (material without autohydrolysis). Pellet production represents 10% of total energy consumed in Scenario 2.

3.4 Economic Evaluation

The project is considered economically viable when the IRR is greater than 15% for a period of 5 years (value in the range of the standard requirements by the financial market [44]). The parameters considered for the analysis are shown in Table 3. It was considered that the plant would operate at 50% capacity in the first year, and at full capacity for the rest of its lifetime (10 years).

The IRR of each scenario was calculated taking into account the xylans conversion of residual hemicellulosic liquor to xylitol and two alternatives of conversion for the residual solid from autohydrolysis (ethanol or pellets).

The alternative of producing xylitol and pellets could mean an attractive option for a small-sized biorefinery project. Xylitol is one of the most interesting products derived from hemicelluloses (by xylose fermentation) [45].

Pellets are an important fuel in emerging markets (Asia and Latin America) with worldwide interest from an energy perspective.

The xylitol and ethanol combination appears as a less attractive alternative, needing to optimize some steps in order to reduce production cost. The results of IRR for the different options are presented in Table 4. The analysis assumes that the raw material is available at the place where the processes are performed and the supply chain costs are included in feedstock cost.

The high investment costs and low market price of ethanol make this alternative less attractive for small scale. The production of xylitol together with pellets

can be considered attractive due to the lower investment cost required for this alternative.

For the profitable production of second-generation ethanol at small scale, it is necessary to optimize the involved processes, e.g., autohydrolysis, evaporation, delignification, and purification, which present high-energy consumption. Another alternative could be the use of lignin as high value-added products, e.g., for antioxidants, resins, and adhesives.

Table 3 Unit prices for bagasse, chemicals, products, energy, labor, and maintenance.

Unit prices at mill gate	
Bagasse (USD t ⁻¹) ^a	7.02
Water (USD m ⁻³) ^b	0.585
Electricity (USD MW.h ⁻¹) ^c	51.5
Labor (USD h ⁻¹) ^d	3.09–4.41 (assumption)
Steam (USD Tn ⁻¹)	30
Maintenance and taxes	8% (of revenue)
Tax rate	35%
Depreciation of Scenario I (USD year ⁻¹)	3,971,450
Depreciation of Scenario II (USD year ⁻¹)	3,155,818
Chemicals for production	
H ₂ SO ₄ (USD kg ⁻¹) ^e	0.04
Ca(OH) ₂ (USD kg ⁻¹) ^e	0.134
Fermentation (USD kg ⁻¹) ^{e, f}	0.11
Enzyme price (USD L ⁻¹) ^g	0.05
Na(OH) (USD kg ⁻¹) ^e	0.53
Products (assumptions)	
Xylitol (USD kg ⁻¹)	8.5
Ethanol (USD L ⁻¹) ^h	1.31
Pellets (USD t ⁻¹)	128.7

^aPrice estimated from the Instituto Nacional de Tecnología Agroindustrial (INTA) [53]; ^bAverage price in Argentina; ^cEnergy cost in Misiones, Argentina; ^dValue depends on the worker position; ^eAverage international price [42]; ^fNutrients, yeast, etc.; ^gEnzyme per liter of ethanol [46]; ^hAverage price of gasoline in Misiones, Argentina.

In a previous study, Clauser *et al.* [25] proposed schemes for xylitol production with MFD or energy generation, obtaining IRR of 8 and 10%, respectively. The alternative of xylitol and pellet production studied in this work shows higher IRR at the same scale (15,000 tons of bagasse).

3.4.1 Production at Different Scales

There are many raw materials that could be processed in a biorefinery. Each of these raw materials has distinctive characteristics and properties. The volumes of ethanol obtained using only the cellulose fraction of the bagasse (20–178 L ton⁻¹, depending on factors such as lignin content of pretreated material and process yield), are between those obtained by Soares and Gouveia [30] using bagasse and by Franceschin *et al.* [44] working with rye straw. When the fraction of pentoses and hexoses are used, the total volume produced could increase to 181–270 L ton⁻¹ [17, 46]. In xylitol production, the obtained results were similar to those obtained by Fatehi *et al.* [27] using a prehydrolysis liquor from kraft-based dissolving pulp at larger scale.

To estimate a profitable processes scale, the capital investment costs, operating costs, and material costs were evaluated at different scales. Equipment and installation costs were estimated using Equation 2. In addition, the operating costs were calculated based on the capacity of production [39].

Investment costs for different alternatives along with the corresponding IRR are presented in Figure 3, which shows that the most attractive alternative is the production of xylitol and pellets, due to its inferior capital investment and good market price. Second-generation ethanol production is not attractive at these scales.

Techno-economic assessments based on the biorefinery concept have increased in recent years. Most studies involved large quantities of raw material for the production of ethanol [46, 47–49], xylitol [27, 44] syrups [50], pellets [51], and other products [6, 25, 44, 48]. Large-scale projects require high amounts of raw materials and significant capital investments. Capital investment for ethanol production at commercial scale are over USD 200 million [47]. Morales-Rodriguez *et al.* [48] have determined production costs between 0.41 and 0.65 USD L⁻¹ of ethanol and 0.82 and

Table 4 Economic results for the scenarios based on 15,000 tons of dry bagasse per year.

Residual solid conversion	Total capital investment (USD)	IRR (% 5 years)*	IRR (% 5 years)**
Xylitol and Pellets	31,558,175	12.5	12.5
Xylitol and Ethanol	39,714,500	8.0	6.7

*Since the mill started to produce. **With an ethanol price equivalent to 0.7 of that of gasoline. Cost of delivery and commercialization of ethanol are not included in the selling price.

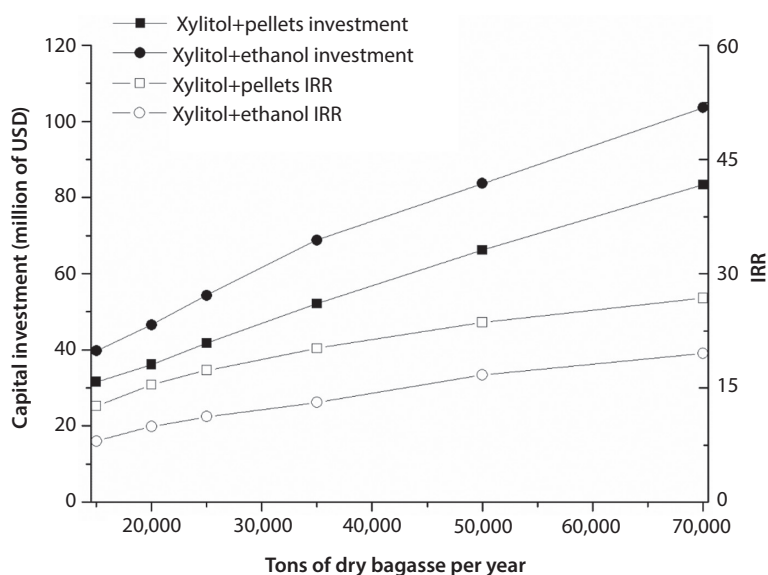


Figure 3 Investment costs and IRR variation for sugarcane bagasse processing in the different studied scenarios.

39.4 USD kg⁻¹ of xylitol, at a scale of 51–57 tons per hour, integrating the energy generated with the residual solids not converted in the process. Kelloway and Daoutidis [6] have evaluated the production of xylitol, formic acid, levulinic acid and others based on a capacity of 1000 tons per day with a NPV of USD 247 million. Using between 125–1,341 tons per day of raw material with production costs between USD 0.36 and 0.68 per kg is attractive for ethanol production alone [46, 49]. For second-generation ethanol, Macrelli *et al.* [52] analyzed the production in different schemes, from a capacity of 74 tons per hour of sugarcane bagasse. It was determined that at the time, the minimum selling price for second-generation ethanol varied between 1.55 and 0.78 USD L⁻¹, depending on the integration of the processes and the use of the residual solid.

The production cost of pellets at a capacity of 22,000 and 44,000 tons per year is between USD 40 and 103 per ton, depending on factors such as raw material price, energy price, etc. [51]; other authors report production costs higher than USD 150 per ton [21]. In order to help the rural areas of the region (which increasingly suffer more economic migration to urban areas), it is necessary to find economic activities that may counteract this situation. Therefore, given that there are small amounts of waste (such as biomass) distributed in the less industrialized rural areas that could be used, this study aims to provide information that would serve as a starting point for future studies in order to reactivate regional economies and generate jobs. The production costs for the processing of 15,000, 50,000 and 70,000 tons per year of dry bagasse are shown in Table 5. These costs include feedstock,

Table 5 Production costs for a capacity of 15,000, 50,000 and 70,000 tons per year of dry bagasse.

Products	Production cost at different scale		
Bagasse processing (t/year)	15,000	50,000	70,000
Ethanol (USD/L)	1.72	1.44	1.38
Xylitol (USD/kg)	5.28	4.30	4.14
Pellets (USD/t)	88.2	66.9	63.8

chemicals, utilities (electricity and steam), depreciation, labor, and maintenance.

There is little decrease in production costs in the studied range of scales, which shows the need for a better integration of processes to reduce production costs. In the case of pellets, the difference in production costs is greater because the inputs and energy involved are lower xylitol and ethanol production. In the scenario of xylitol and ethanol production, numerous inputs, operations, reactions, and large amounts of energy are involved, which again demonstrates the need for integration of processes and the use of all fractions of the raw material (hemicelluloses, cellulose and lignin) to obtain attractive biorefinery schemes, achieving high-value products at commercial cost.

The improvement in the IRR at different scales is usual in capital-intensive plants for biomass processing (capital cost per unit of output decreases as plant capacity increases) [21].

In addition, the analysis for each scenario shows that production costs are higher than those obtained

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

by other authors for biorefineries at larger scales. However, a significant decrease in production costs could be achieved through the further integration of processes and using all currents and by-products (e.g., lignin for energy generation, energy recovery in the different stages, others). This would allow profitable production of added-value products with lower amounts of raw material, which could be profitable, pulling progress to rural areas.

4 CONCLUSIONS

A technical-economic analysis of small-scale biorefineries to produce value-added biobased products from sugarcane bagasse was assessed. The internal rate of return (IRR) was used to compare the profitability of potential investments in the different proposed scenarios. The scale processing 15,000 tons of bagasse per year presented low IRRs: 8% for xylitol + ethanol and 12.5% for xylitol + pellets. However, higher IRR values were obtained by increasing the scale to 70,000 tons per year of bagasse. Simultaneous production of xylitol and pellets is an interesting option when processing more than 20,000 tons per year of bagasse, whereas xylitol and ethanol production need to process 50,000 tons per year to be rentable. In addition, the improvement of the energy integration of the processes and the addition of value to all fractions of the material, make possible the reduction of production costs of products that can compete in different markets.

ACKNOWLEDGMENT

The authors acknowledge the PROVALOR-CYTED network (Value-Added Products from Forest- and Agro-industrial Residues), the Universidad de la República (UDELaR, Uruguay), the Universidad Nacional de Misiones (UNaM) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for the financial support.

REFERENCES

1. M. Bruins and J. Sanders, Perspective: Small-scale processing of biomass for biorefinery. *Biofuels, Bioprod. Biorefin.* **6**(3), 135–145 (2011).
2. CONAB, Acompanhamento da Safra Brasileira de Cana de Açúcar, Ministério da Agricultura (2015). [Online]. Available: <http://www.conab.gov.br/>. [Accessed: 03-Feb-2016].
3. S.S. da Silva and A.K. Chandel (Eds.), *Biofuels in Brazil: Fundamental Aspects, Recent Developments, and Future Perspectives*, Springer International Publishing, Switzerland (2014).
4. INTA, Caña de azúcar: símbolo de identidad cultural y desarrollo local (2013). [Online]. Available: <http://intainforma.inta.gov.ar/?p=17968>. [Accessed: 15-Feb-2016].
5. M.E. Vallejos, M.D. Zambon, M.C. Area, and A.A. da Silva Curvelo, Low liquid–solid ratio (LSR) hot water pretreatment of sugarcane bagasse. *Green Chem.* **14**(7), 1982–1989 (2012).
6. A. Kelloway and P. Daoutidis, Process synthesis of biorefineries: Optimization of biomass conversion to fuels and chemicals. *Ind. Eng. Chem. Res.* **53**(13), 5261–5273 (2013).
7. T.L. De Albuquerque, I.J. da Silva, G.R. de Macedo, and M.V.P. Rocha, Biotechnological production of xylitol from lignocellulosic wastes: A review. *Process Biochem.* **49**(11), 1779–1789 (2014).
8. L. Venkateswar Rao, J.K. Goli, J. Gentela, and S. Koti, Bioconversion of lignocellulosic biomass to xylitol: An overview. *Bioresour. Technol.* **213**, 299–310 (2016).
9. J. Baeyens, Q. Kang, L. Appels, R. Dewil, Y. Lv, and T. Tan, Challenges and opportunities in improving the production of bio-ethanol. *Prog. Energy Combust. Sci.* **47**, 60–88 (2015).
10. C.A. Cardona, J.A. Quintero, and I.C. Paz, Production of bioethanol from sugarcane bagasse: Status and perspectives. *Bioresour. Technol.* **101**(13), 4754–4766 (2010).
11. M.J. Taherzadeh and K. Karimi, Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review. *Int. J. Mol. Sci.* **9**, 1621–1651 (2008).
12. S.I. Mussatto (Ed.), *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*, Elsevier, Oxford (2016).
13. C.R. Soccol, L.P. Vandenberghe, A.B. Medeiros, S.G. Karp, M. Buckeridge, L.P. Ramos, A.P. Pitarello, V. Ferreira-Leitão, L.M. Gottschalk, M.A. Ferrara, E.P. da Silva Bon, L.M. de Moraes, A. Araújo Jde, and F.A. Torres, Bioethanol from lignocelluloses: Status and perspectives in Brazil. *Bioresour. Technol.* **101**(13), 4820–4825 (2010).
14. K. Olofsson, M. Bertilsson, and G. Lidén, A short review on SSF – An interesting process option for ethanol production from lignocellulosic feedstocks. *Biotechnol. Biofuels* **1**(1), 7 (2008).
15. M. Holtzapple, M. Cognata, Y. Shu, and C. Hendrickson, Inhibition of *Trichoderma reesei* cellulase by sugars and solvents. *Biotechnol. Bioeng.* **36**(3), 275–287 (1990).
16. X. Zhao, G.K. Moates, A. Elliston, D.R. Wilson, M.J. Coleman, and K.W. Waldron, Simultaneous saccharification and fermentation of steam exploded duckweed: Improvement of the ethanol yield by increasing yeast titre. *Bioresour. Technol.* **194**, 263–269 (2015).
17. H.B. Aditiya, T.M.I. Mahlia, W.T. Chong, H. Nur, and A.H. Sebayang, Second generation bioethanol production: A critical review. *Renew. Sustain. Energy Rev.* **66**, 631–653 (2016).
18. M. Peksa-Blanchard, P. Dolzan, A. Grassi, J. Heinimö, M. Junginger, T. Ranta, and A. Walter, Global wood pellets markets and industry: Policy drivers, market status and raw material potential, IEA Bioenergy Task 40 (2007).
19. V. Karkania, E. Fanara, and A. Zabaniotou, Review of sustainable biomass pellets production – A study for

- agricultural residues pellets' market in Greece. *Renew. Sustain. Energy Rev.* **16**(3), 1426–1436 (2012).
20. A. Sultana and A. Kumar, Ranking of biomass pellets by integration of economic, environmental and technical factors. *Biomass Bioenerg.* **39**, 344–355 (2012).
 21. A. Sultana, A. Kumar, and D. Harfield, Development of agri-pellet production cost and optimum size. *Bioresour. Technol.* **101**(14), 5609–5621 (2010).
 22. Z. Tooyserkani, L. Kumar, S. Sokhansanj, J. Saddler, X.T. Bi, C.J. Lim, A. Lau, and S. Melin, SO₂-catalyzed steam pretreatment enhances the strength and stability of softwood pellets. *Bioresour. Technol.* **130**, 59–68 (2013).
 23. M.E. Vallejos, F.E. Felissia, J. Kruyeniski, and M.C. Area, Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. *Ind. Crops Prod.* **67**, 1–6 (2015).
 24. Y. Lei, S. Liu, J. Li, and R. Sun, Effect of hot-water extraction on alkaline pulping of bagasse. *Biotechnol. Adv.* **28**(5), 609–612 (2010).
 25. N.M. Clauser, S. Gutiérrez, M.C. Area, F.E. Felissia, and M.E. Vallejos, Small-sized biorefineries as strategy to add value to sugarcane bagasse. *Chem. Eng. Res. Des.* **107**, 137–146 (2015).
 26. Y. Ping, H.Z. Ling, G. Song, and J.P. Ge, Xylitol production from non-detoxified corncob hemicellulose acid hydrolysate by *Candida tropicalis*. *Biochem. Eng. J.* **75**, 86–91 (2013).
 27. P. Fatehi, L. Catalan, and G. Cave, Simulation analysis of producing xylitol from hemicelluloses of pre-hydrolysis liquor. *Chem. Eng. Res. Des.* **92**(8), 1563–1570 (2014).
 28. M.E. Vallejos, M.D. Zambon, M.C. Area, and A.A.D.S. Curvelo, Low liquid-solid ratio fractionation of sugarcane bagasse by hot water autohydrolysis and organosolv delignification. *Ind. Crops Prod.* **65**, 349–353 (2014).
 29. T.L. Junqueira, M.O.S. Dias, O. Cavalett, C.D.F. Jesus, M.P. Cunha, C.E.V. Rossell, M. F.R. Maciel, and A. Bonomi, Economic and environmental assessment of integrated 1st and 2nd generation sugarcane bioethanol production evaluating different 2nd generation process alternatives, in *22nd European Symposium on Computer Aided Process Engineering*, D. Bogle and M. Fairweather (Eds.), 1st ed., vol. 3, no. 3, pp. 177–181, Elsevier: London (2012).
 30. M.L. Soares and E.R. Gouveia, Influence of the alkaline delignification on the simultaneous saccharification and fermentation (SSF) of sugar cane bagasse. *Bioresour. Technol.* **147**, 645–648 (2013).
 31. G.J.M. Rocha, A.R. Gonçalves, S.C. Nakanishi, V.M. Nascimento, and V.F.N. Silva, Pilot scale steam explosion and diluted sulfuric acid pretreatments: Comparative study aiming the sugarcane bagasse saccharification. *Ind. Crops Prod.* **74**, 810–816 (2015).
 32. H. Sixta (Ed.), *Handbook of Pulp*, Wiley, New York (2006).
 33. United Nations Industrial Development Organization, The Economic and Financial Analysis Study for the Jute/Kenaf Pulp Manufacturing (2004).
 34. J.G. Brizuela, Pellets para combustión a partir de residuos foresto-industriales, Universidad Nacional de Misiones (2015).
 35. F. Shafizadeh, K. Sarkanen, and D. Tillman (Eds.), *Thermal Uses and Properties of Carbohydrates and Lignins*, Academic Press, USA (1976).
 36. P.R. Stuart and M.M. El-Halwagi (Eds.), *Integrated Biorefineries, Design, Analysis and Optimization*, CRC Press, Boca Raton (2014).
 37. J. Sadhukhan, K.S. Ng, and E. Martinez, *Biorefineries and Chemical Processes*, Wiley, New York (2014).
 38. J. Harmsen, *Industrial Process Scale-up: A Practical Innovation Guide from Idea to Commercial Implementation*, Elsevier, UK (2013).
 39. W.D. Seider, J.D. Seader, and D.R. Lewin, *Product and Process Design Principles – Synthesis, Analysis, and Evaluation*, pp. 505–556, John Wiley & Sons, Inc., New York (2003).
 40. OpenOffice, Apache Openoffice Calc (2015). [Online]. <https://www.openoffice.org/es/producto/calc.html>.
 41. C.J. Geankoplis, *Procesos de transporte y operaciones unitarias*, 3ª ed., Prentice-Hall International, Mexico (1998).
 42. H.S. Hörhammer, T.H. Treasure, R.W. Gonzalez, and A.R.P. Van Heiningen, Larch biorefinery: Technical and economic evaluation. *Ind. Eng. Chem. Res.* **53**, 1206–1213 (2014).
 43. S. Misra, P. Gupta, S. Raghuwanshi, K. Dutt, and R.K. Saxena, Comparative study on different strategies involved for xylitol purification from culture media fermented by *Candida tropicalis*. *Sep. Purif. Technol.* **78**(3), 266–273 (2011).
 44. G. Franceschin, M. Sudiro, T. Ingram, I. Smirnova, G. Brunner, and A. Bertucco, Conversion of rye straw into fuel and xylitol: A technical and economical assessment based on experimental data. *Chem. Eng. Res. Des.* **89**(6), 631–640 (2011).
 45. S.S. da Silva and A.K. Chandel (Eds.), *D-Xylitol: Fermentative Production, Application and Commercialization*, Springer, Berlin (2012).
 46. M.O.S. Dias, T. L. Junqueira, O. Cavalett, M. P. Cunha, C. D. F. Jesus, P. E. Mantelatto, C. E. V. Rossell, R. M. Filho, and A. Bonomi, Cogeneration in integrated first and second generation ethanol from sugarcane. *Chem. Eng. Res. Des.* **91**(8), 1411–1417 (2013).
 47. T.R. Brown and R.C. Brown, A review of cellulosic biofuel commercial-scale projects in the United States. *Biofuels, Bioprod. Biorefin.* **6**(3), 246–256 (2012).
 48. R. Morales-Rodriguez, E.S. Perez-Cisneros, J.A. de Los Reyes-Heredia, and D. Rodriguez-Gomez, Evaluation of biorefinery configurations through a dynamic model-based platform: Integrated operation for bioethanol and xylitol co-production from lignocellulose. *Renew. Energy* **89**, 135–143 (2016).
 49. J.A. Quintero, J. Moncada, and C.A. Cardona, Techno-economic analysis of bioethanol production from lignocellulosic residues in Colombia: A process simulation approach. *Bioresour. Technol.* **139**, 300–307 (2013).
 50. J.A. Dávila, V. Hernández, E. Castro, and C.A. Cardona, Economic and environmental assessment of syrup production. Colombian case. *Bioresour. Technol.* **161**, 84–90 (2014).
 51. A. Uasuf, and G. Becker, Wood pellets production costs and energy consumption under different framework

- 1 conditions in Northeast Argentina. *Biomass Bioenerg.*
2 35(3), 1357–1366 (2011).
3 52. S. Macrelli, J. Mogensen, and G. Zacchi, Techno-economic
4 evaluation of 2nd generation bioethanol production from
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
- sugar cane bagasse and leaves integrated with the sugar-
based ethanol process. *Biotechnol. Biofuels* 5(1), 22 (2012).
53. INTA, Planilla de Precios Forestales (2013). [Online].
<http://inta.gob.ar/>. [Accessed: 01-Feb-2016].