Bioresource Technology 142 (2013) 390–399

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Utilization of pentoses from sugarcane biomass: Techno-economics of biogas vs. butanol production

Adriano Pinto Mariano [a,*], Marina O.S. Dias [b], Tassia L. Junqueira [a,b], Marcelo P. Cunha [b], Antonio Bonomi [a,b], Rubens Maciel Filho [a,b]

[a] Laboratory of Optimization, Design and Advanced Control (LOPCA), School of Chemical Engineering – University of Campinas (UNICAMP), Av. Albert Einstein 500, CEP 13083-852 Campinas, SP, Brazil

[b] Laboratório Nacional de Ciência e Tecnologia do Bioetanol – CTBE/CNPEM, Caixa Postal 6170, CEP 13083-970 Campinas, SP, Brazil

HIGHLIGHTS

- Greenfield projects of a second-generation sugarcane biorefinery were evaluated.
- Pentoses from sugarcane biomass were used either for biogas or *n*-butanol production.
- Production of *n*-butanol and acetone led to increased and diversified revenues.
- Energy efficiency of the butanol plant affected power and ethanol production.
- Energy reduction in the butanol plant enhanced the profitability of the biorefinery.

ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form 14 May 2013
Accepted 15 May 2013
Available online 23 May 2013

Keywords:
Biorefinery
Sugarcane
Pentoses
Biogas
Butanol

ABSTRACT

This paper presents the techno-economics of greenfield projects of an integrated first and second-generation sugarcane biorefinery in which pentose sugars obtained from sugarcane biomass are used either for biogas (consumed internally in the power boiler) or *n*-butanol production via the ABE batch fermentation process. The complete sugarcane biorefinery was simulated using Aspen Plus®. Although the pentoses stream available in the sugarcane biorefinery gives room for a relatively small biobutanol plant (7.1–12 thousand tonnes per year), the introduction of butanol and acetone to the product portfolio of the biorefinery increased and diversified its revenues. Whereas the IRR of the investment on a biorefinery with biogas production is 11.3%, IRR varied between 13.1% and 15.2% in the butanol production option, depending on technology (regular or engineered microorganism with improved butanol yield and pentoses conversion) and target market (chemicals or automotive fuels). Additional discussions include the effects of energy-efficient technologies for butanol processing on the profitability of the biorefinery.

1. Introduction

In Brazil, the great majority of the current annual bioethanol production of about 25 billion liters is based on the fermentation of sugars (glucose + fructose) obtained from the sugarcane juice in mills called first-generation (1G) biorefineries. Basically, there are two biorefinery models, namely annexed plants and autonomous distilleries. In the former, sugars from the sugarcane juice are converted to ethanol and food-grade sugar, and the sugarcane bagasse is burnt to generate steam and power. This model accounts for approximately 70% of the Brazilian sugarcane biorefineries (Cavalett et al., 2012). In the latter, on the other hand, sugar is not produced. In both cases, if efficient high-pressure boilers (65–90 bar) are employed in the cogeneration system, surplus electricity can be sold to the power grid. Still valid for both models, the concept of second-generation (2G) biorefineries is defined by the utilization of fermentable sugars extracted from the lignocellulosic portion of the sugarcane plant, such as the bagasse, in order to produce ethanol.

The integration of second-generation units with conventional first-generation biorefineries, in contrast to stand-alone second-generation units, has the potential to offer significant economic advantages since important operations (concentration, fermentation, distillation and cogeneration) and feedstock (sugarcane bagasse is already available at plant site) may be shared between both plants (Dias et al., 2012). Furthermore, extending to the technical side, the effects on fermentation yields of inhibitors gener-

* Corresponding author. Present address: Department of Chemical Engineering, École Polytechnique de Montréal C.P. 6079, Succ. Centre-Ville, Montreal, QC H3C 3A7, Canada. Tel.: +1 514 340 4711x3424; fax: +1 514 340 5150.

E-mail addresses: adriano.mariano@polymtl.ca, adrianomariano@yahoo.com.br (A.P. Mariano).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.05.052

ated during biomass pretreatment can be minimized, if not eliminated, by mixing the hydrolyzed liquor with sugarcane juice. However, an important fraction (~25%) of the sugars available in the bagasse, the pentose sugars, cannot be fermented by the yeast *Saccharomyces cerevisiae* employed in sugarcane biorefineries. Although engineered microorganisms able to ferment pentoses to ethanol have been developed, to date none of them could outperform the high fermentation yield and productivity achieved with *S. cerevisiae* (Chandel et al., 2011). In face of this limitation, the biodigestion of the pentose sugars for the production of biogas is an interesting solution to increase ethanol production (Rabelo et al., 2011). The logic is straightforward. Since bagasse is used to produce steam and power, the amount of bagasse available as feedstock for ethanol production depends on the thermal energy consumption of the biorefinery. By supplementing the cogeneration system with biogas, this additional source of energy increases the availability of bagasse for ethanol production.

Alternatively, pentose sugars could be used for the production of added-value chemicals or advanced biofuels, resulting in increased revenues. Particularly, *n*-butanol, hereafter simply butanol, has attracted the attention of investors due to its potential use as a drop-in biofuel and demand by the chemical market. The opportunities around butanol, as phrased by Mascal (2012), are extraordinarily diverse, and have a real potential to permanently impact the renewable energy and materials landscape. Moreover, in the biorefinery context, butanol production from pentose sugar rich hemicellulose streams resulting from agricultural and wood processing plants is an attractive option given the broad substrate ranges of solventogenic clostridia, including pentose sugars (Green, 2011). For example, from the fractionation of corn stover, the Chinese company Jilin Songyuan Laihe Chemicals is producing cellulose as raw material for paper, polyether polyol and phenolic resins from lignin, and butanol from the hemicellulose fraction (http://www.laihe.net/en.aspx).

Nevertheless, a technical aspect related to fermentation processes in general, and markedly present in the butanol processing, may have an important effect on the availability of biomass for ethanol production. The fermentation to produce butanol is characteristically much diluted and, consequently, steam-consuming operations such as sterilization of the sugar solution and downstream product recovery (distillation) are energy-intensive (Vane, 2008; Mariano and Maciel Filho, 2012). In this manner, by opting to use the pentoses stream for butanol production, the 2G ethanol production is expected to decrease due to (i) increased thermal energy consumption in the biorefinery, and (ii) absence of the additional biogas energy stream. In face of these technical aspects, critical questions must be addressed in order to evaluate the economics of the two competing options for pentoses utilization considered in this study. Would the selling of additional products, butanol and the by-product acetone, bring economic advantages despite the reduction in second-generation ethanol production? What is the effect of the butanol plant on the excess power generated by the biorefinery? And perhaps most importantly, given that a great deal of effort has been put into developing energy-efficient technologies for butanol processing, how much would a reduction in steam consumption in the butanol plant affect the profitability of the biorefinery? To answer these questions, this paper presents a technical and economic assessment of greenfield projects of an integrated first and second-generation sugarcane biorefinery (annexed plant model) in which pentose sugars obtained from sugarcane biomass are used either for biogas or butanol production. The biorefinery concepts were assessed with regard to important technical performance parameters, such as biomass utilization breakdown (cogeneration and ethanol production), products output, steam and power consumption, and wastewater footprint. Revenue diversification, steam consumption in the butanol plant, and technology advances in butanol processing guided the discussions of the economic analysis.

2. Methods

2.1. Process description

In the base case scenario, the second-generation ethanol production is integrated to an annexed plant with a processing capacity of 503 tonnes of sugarcane stalks (TC) per hour in 167 days per year (~2 million tonnes of sugarcane/year). After cleaning and crushing the stalks, 122 kg of bagasse in dry basis are produced per TC (lower heating value – LHV of bagasse with 50 wt.% moisture content is 7.5 MJ/kg). Additionally, 50% of the sugarcane straw (tops and leaves) produced in the field is transported to the biorefinery, i.e. 68 dry kg/TC (LHV of straw with 15 wt.% moisture content is 15.1 MJ/kg). Five percent of the bagasse is stockpiled for boiler start-ups. In this manner, 92 dry tonnes of biomass per hour (63% bagasse; 37% straw) are available for the biorefinery. In dry basis, the contents of cellulose, hemicellulose, and lignin in the biomass are 47, 28, 25 wt.%, respectively (Dias et al., 2011a, 2012).

The juice extracted from the sugarcane stalks (133 kg sucrose/TC + 6 kg reducing sugars/TC) is split into two equal streams used for the production of sugar and anhydrous ethanol (99.5 wt.%). Molasses (16 kg sucrose/TC + 3 kg reducing sugars/TC), the concentrated residual solution obtained after sugar crystallization, is also used for ethanol production. Steam (12, 6, 2.5 bar) and power are obtained from the combustion of sugarcane bagasse and sugarcane straw in the cogeneration system. In accordance with the current trend for new plants in Brazil, the cogeneration system of the biorefinery has a 90-bar boiler (86% thermal efficiency in LHV basis) integrated with back pressure turbines. This boiler is more efficient than the traditional 22-bar boilers (75% thermal efficiency) and allows for an excess of power, which is sold to the grid. The amount of bagasse and straw sent for cogeneration is determined by the steam consumption of the biorefinery. Thus, lower steam demand in the production processes leads to higher amounts of bagasse and straw available for second-generation ethanol production. Surplus bagasse and straw are converted into fermentable sugars through pretreatment (steam explosion, 12-bar steam, 190 °C, 15 min) and enzymatic hydrolysis. By steam exploding the biomass, part of the hemicellulose is converted into pentoses and, simultaneously, cellulose becomes available to enzymatic hydrolysis (Martín et al., 2002). In this operation, hemicellulose and cellulose hydrolysis yields are, respectively, 70% and 2%. In the enzymatic hydrolysis step, it was assumed a hydrolysis yield of 60% and solids loading of 10 wt.% according to the current technology for lignocellulosic ethanol production (Dias et al., 2011b). The hexose fraction obtained in the hydrolysis is mixed with sugarcane juice and, after concentration in multiple effect evaporators, fermented to ethanol. The pentose fraction is anaerobically digested to produce biogas, which is burnt in the cogeneration system. Unreacted solids obtained after filtration of the hydrolysis products are also used as fuel in the boiler, along with straw and bagasse. For the different fuels, boiler efficiency was assumed to be 86%. In the competing scenario, the same design is considered, however, the pentose fraction is sent to a butanol plant integrated to the biorefinery. This plant produces butanol along with the by-products acetone and hydrous ethanol (85 wt.%). A block flow diagram with the major processing steps and products of the biorefinery, along with the alternative uses for pentoses, is shown in Fig. 1.

Process parameters for the ethanol, sugar and cogeneration plants are representative of Brazilian industrial large scale plants (over 1 million L of ethanol per day) and were obtained from the literature (Ensinas et al., 2007; Macedo et al., 2008) and interviews

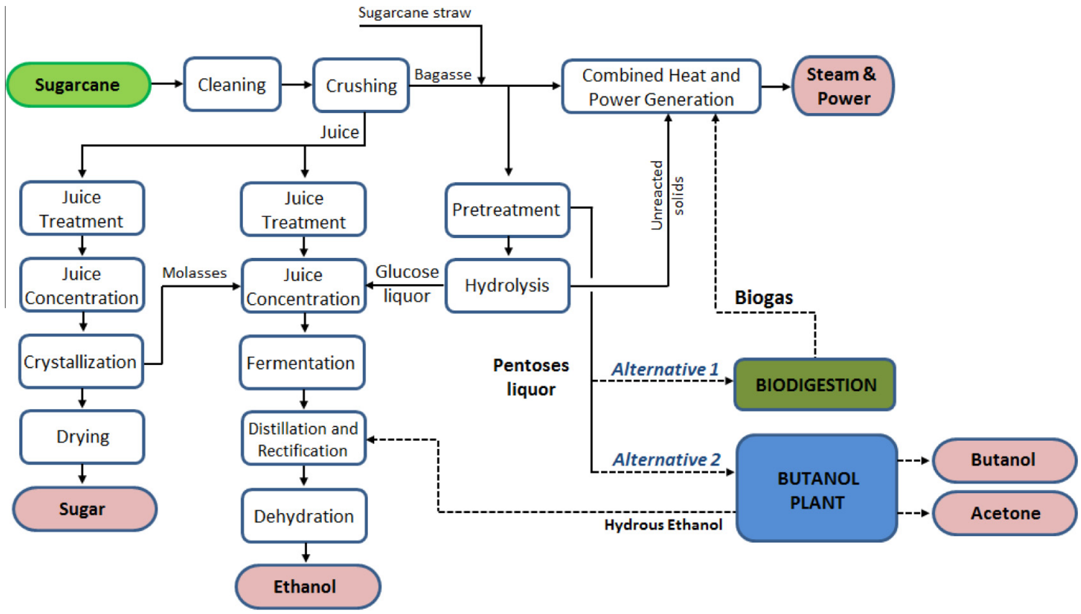

Fig. 1. Schematic diagram of an integrated 1G–2G sugarcane biorefinery with sugar, power, and ethanol production (ethanol from sugarcane juice and hexoses from bagasse). Alternatives for pentoses use: (1) biodigestion of pentoses – resulting biogas is used for power and steam generation; (2) fermentation of pentoses for production of butanol, and the by-products acetone and hydrous ethanol.

with specialists. Since there is no industrial-scale 2G ethanol plant currently in Brazil, parameters for biomass pretreatment and enzymatic hydrolysis were obtained from the literature (Leibbrandt et al., 2011; Ojeda et al., 2011) and information from specialists. It should be noted that the integrated 1G-2G production process considers the fermentation of mixed sugarcane juice and hydrolyzed glucose liquor. Possible impacts on fermentation yields due to the presence of potential inhibitors generated during pretreatment reactions were not considered given that their concentration on the fermentation media would be very low. Thus, the same conversion that is observed nowadays in first generation ethanol industrial plants (conversion of 90% of the C6 sugars to ethanol) was assumed. Ethanol is dehydrated in molecular sieves, and electric drives are employed in the sugarcane preparation and juice extraction systems. Additionally, it was assumed a 20% reduction on process steam (2.5 bar) consumption in the ethanol and sugar plants, which may be achieved by means of process integration (Dias et al., 2011a). Further details on the ethanol, sugar, and cogeneration processes may be found in previous studies (Dias et al., 2011b, 2012; Cavalett et al., 2012; CTBE, 2012).

The pentoses liquor stream contains 142 g sugars/L (4.5% glucose; 10.9% sucrose – resulting from inefficiencies in the extraction of juice from the bagasse; 84.6% xylose). In the base-case scenario, the COD removal efficiency in the biodigestion reactor is 70%. This assumption is based on values obtained in the sugarcane industry for vinasse (stillage) biodigestion, according to a personal communication with Dedini, a Brazilian company who manufactures equipment for sugarcane biorefineries. Biodigestion is conducted at 55 °C, yielding 0.35 Nm^3 biogas per kg of reducing sugars. The LHV of biogas is 21.3 MJ/Nm^3. In the competing scenario, the pentoses liquor stream is diluted to 50–60 g/L sugars (Fig. 2a) because butanol inhibition prevents the use of more concentrated sugar solutions (Roffler et al., 1987). The diluted feed stream is continuously sterilized (100 °C) and sent to fermentation unit (Fig. 2b). The fermentation process using solventogenic Clostridium cells consists of a continuous cell production stage (seed fermentors) and a second batchwise fermentation stage where acetone, butanol, ethanol (ABE) are produced (Afschar et al., 1990). As such, the pentoses liquor stream is split in two streams (volume ratio 1.4:10) and the smaller is fed to the seed fermentors after being diluted to 20 g/L and sterilized at 130 °C (2.5-bar steam). The batch fermentors are operated at 32 °C on a staggered schedule and inoculated with actively growing cells. Main performance parameters of the fermentation stage are presented in Table 1 according to a regular and a mutant microorganism with improved butanol yield and pentoses conversion. These parameters are based on experimental data obtained from different studies on the fermentation of hydrolysates of different biomass feedstocks to ABE (Yu et al., 1984; Wayman and Yu, 1985; Marchal et al., 1986; Ezeji et al., 2007; Ezeji and Blaschek, 2008; Qureshi et al., 2010; Liu et al., 2010).

The separation of the fermentation products (ABE) is conducted in a series of five continuous distillation columns (2.5-bar steam), with the last two responsible for the separation of butanol from water (Fig. 2c) (Roffler et al., 1987). The water stream is recycled to the fermentation unit for dilution of the C5 stream, and the hydrous ethanol stream is dehydrated in the distillation unit of the ethanol plant. The stillage (vinasse) from both ethanol and butanol plants are combined and, without any previous treatment, used for the irrigation of sugarcane fields. A detailed description of the distillation unit can be found in Mariano et al. (2011).

2.2. Process simulation

The integrated 1G-2G sugarcane biorefinery, as depicted in Fig. 1, was simulated in Aspen Plus® (Aspentech, v. 7.1). The simulation of the ethanol (1G and 2G) and sugar plants, the co-generation system, and the biodigestion unit was developed previously and is part of the Virtual Sugarcane Biorefinery (VSB) created by the Technological Assessment Program of the Brazilian Bioethanol Science and Technology Laboratory (CTBE). A comprehensive description of the parameters adopted in the construction of the VSB can be found in CTBE (2012) and Dias et al. (2011a).

The Aspen Plus model of the butanol plant (fermentation and distillation units) was developed in this work based on laboratory-scale experiments (Yu et al., 1984; Wayman and Yu, 1985; Marchal et al., 1986; Ezeji et al., 2007; Ezeji and Blaschek, 2008; Qureshi et al., 2010; Liu et al., 2010) and process configurations reported in the literature (Roffler et al., 1987; Afschar et al., 1990).

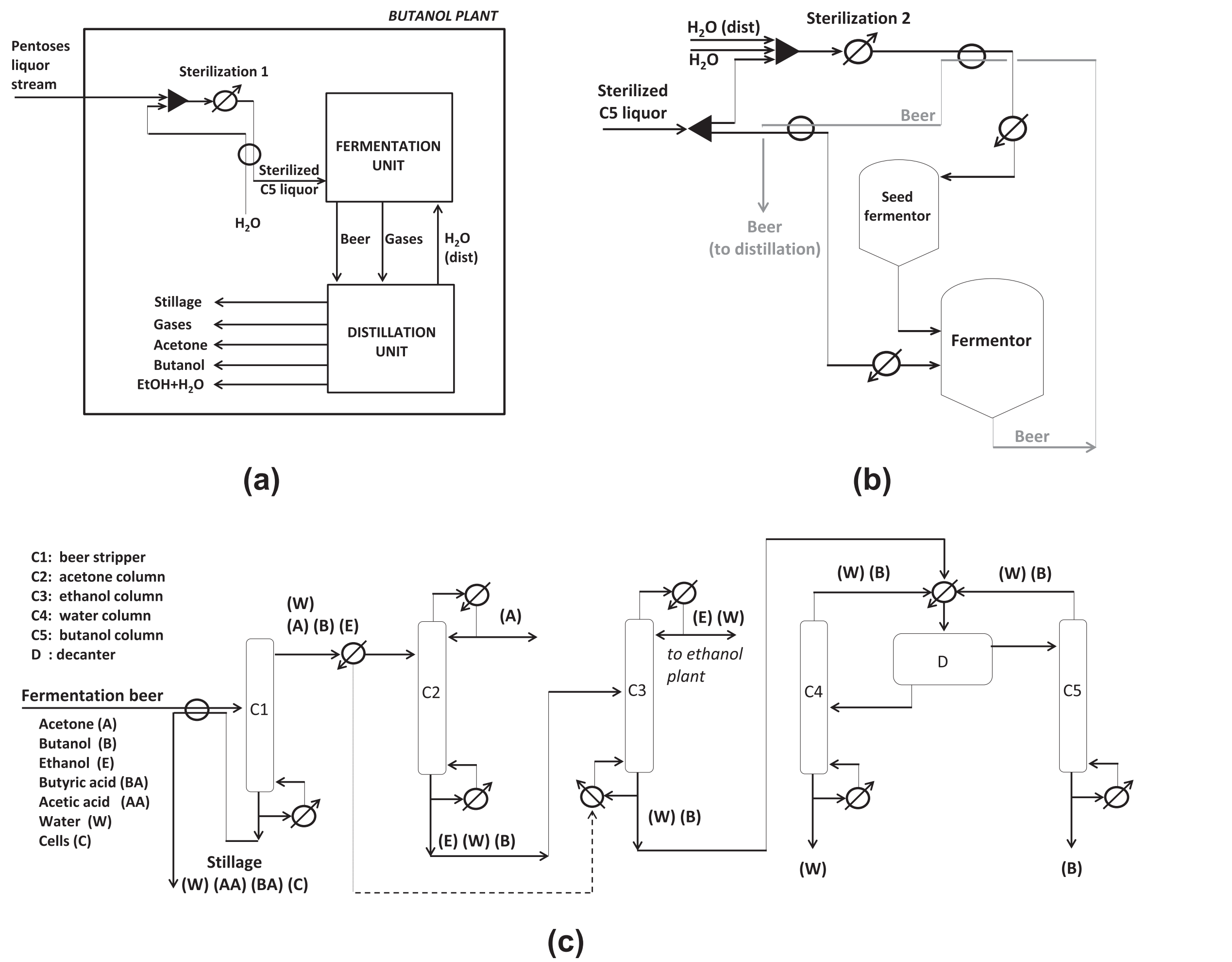

Fig. 2. Butanol plant (fed with pentose sugars from sugarcane biomass) simulated in Aspen Plus®. (a) Hierarchy blocks corresponding to fermentation and distillation units inserted in the Virtual Sugarcane Biorefinery (VSB, developed by CTBE). (b) Fermentation unit. (c) Distillation unit.

Table 1
Main performance parameters of the fermentation unit of the butanol plant.

Parameter	Regular strain (RS)	Mutant strain (MS)
Total conversion of hexoses (%)	95	95
Total conversion of pentoses (%)	80	90
Mass yield from both C6 and C5 sugars (w/w)		
Butanol	0.20	0.30
Acetone	0.10	0.08
Ethanol	0.02	0.01
Acetic acid	0.02	0.01
Butyric acid	0.01	0.01
Cells	0.07	0.07

Unit operations that represent the butanol plant were included in the VSB through two hierarchy blocks corresponding to fermentation and distillation units (Fig. 2a). Regarding the former, two technological scenarios were created in order to evaluate the economics of butanol production from pentoses: (i) fermentation with a regular *Clostridium* species (RS), and (ii) fermentation with a mutant Clostridium strain (MS) with improved butanol yield and pentoses conversion (Table 1). For this, a stoichiometric reactor model (RStoic) was used to simulate the seed and batch fermentors, considering the conversion of glucose and xylose to produce ABE, acetic and butyric acid, and cells according to the fermentation parameters presented in Table 1. Distillation columns in the second hierarchy block were simulated using the RadFrac model. Design specifications and operating conditions considered in this block can be found in Mariano et al. (2011). The flowsheets of the fermentation and distillation units simulated in Aspen Plus® are shown in Fig. 2b and c, respectively.

2.3. Economic analysis

A discounted cash flow analysis was used to calculate the Internal Rate of Return (IRR) of the base (biogas production) and competing (butanol production) case scenarios in the Brazilian context. Regarding the competing case, four scenarios involving fermentation technologies (regular and mutant microorganism with improved butanol yield and pentoses conversion) and target markets (chemicals and automotive fuels) were assessed. Table 2 summarizes the scenarios considered for the economic analysis.

All scenarios are greenfield projects and investment cost regarding the base case scenario was estimated by CTBE (2012) based on data provided by UNICA (Brazilian Sugarcane Industry Association) and Dedini. Total equipment cost (TEC) for the butanol plant was estimated by factoring the values reported by Roffler et al. (1987) according to the capacity power law expression (changes in equipment capacity were correlated to costs considering a coefficient of 0.7). The scaled cost was then indexed to a year 2011 US dollar value using the Chemical Engineering Plant Cost

Table 2
Scenarios evaluated in the economic analysis.

Scenario	Definition
BIO-G	Biogas production from pentose sugars
RS-C	Butanol production from pentose sugars. Regular Clostridium strain. Butanol is commercialized as a chemical
MS-C	Butanol production from pentose sugars. Mutant Clostridium strain. Butanol is commercialized as a chemical
RS-F	Butanol production from pentose sugars. Regular Clostridium strain. Butanol is commercialized as an automotive fuel
MS-F	Butanol production from pentose sugars. Mutant Clostridium strain. Butanol is commercialized as an automotive fuel

Index. For the calculation of the total capital investment (TCI) of the butanol plant, an installation factor of 3.0 (across all pieces of equipment) and a location factor of 0.6 were assumed. Thus, TCI was given by TEC × installation factor × location factor.

The following assumptions were adopted for the discounted cash flow analysis: construction and start-up in 2 years; production length of 25 years with an operating factor of 167 days/year (this is an average for sugarcane biorefineries in Sao Paulo State and subject to variations mainly due to weather conditions, which determines the extension of the sugarcane crop season); no subsidies on capital investment costs; 100% of nominal capacity in the first year of production; no debt and 100% equity; 34.65% tax rate (income and social contributions); 10-year linear depreciation; no scrap value; no premium on green products; working capital as 2% of capital investment; and the 2011 average US Dollar to Brazilian Real exchange rate (US$ 1.00 = R$ 1.64). Table 3 summarizes the prices (baseline values) assumed for raw materials and products. It should be noted that for the scenarios targeting the fuels market (RS-F and MS-F), butanol price is based on its energy content and the quotation of anhydrous ethanol.

A sensitivity analysis was conducted on the following key parameters: investment costs (1G–2G ethanol-sugar plant, biodigestion unit, butanol plant) and prices of raw materials and products. In relation to the baseline values (Tables 3 and 6), these parameters were varied by ±10% according to a factorial design (Plackett–Burman design), which was used to determine, using the software Statistica® (Statsoft Inc., v. 7.0), the effects of the economic parameters on IRR.

Due to uncertainty of the economic parameters, an economic risk analysis was conducted using Monte Carlo simulation in Microsoft Excel®. Probability distribution were defined for the economic parameters assuming normal distribution for variables with historical record and triangular distribution otherwise (Table 4). Five thousand iterations were run using the probability distributions and, for each iteration, parameters were randomly varied according to the defined distribution for each value, resulting in probability curves for IRR. In the case of correlated variables (prices of sugarcane, sugar, ethanol, and butanol as a biofuel), their expected values were calculated using the same Excel-generated random numbers. In this manner, these variables had similar oscillation patterns throughout the simulation. Results of the Monte Carlo simulation were used to determine the probability of IRR be greater than 12%.

Table 3
Prices (baseline values) used in the economic analysis.

Parameter	Value
Sugarcane (US$/wet tonne)[a,b]	27.26
Sugarcane straw (US$/wet tonne)[c]	18.29
Microorganism license (MS) (US$/L butanol)[d]	0.016
Enzyme – hydrolysis (US$/L lignocellulosic ethanol)[e]	0.12
Anhydrous ethanol (US$/L)[a,f]	0.66
Sugar (US$/kg)[a,g]	0.48
Power (US$/MWh)[h]	60.98
n-Butanol (chemical market) (US$/kg)[a,i]	1.65
n-Butanol (fuels market) (US$/kg)[j]	1.03
Acetone (US$/kg)[a,k]	1.16

[a] 6-Year moving average of prices (December 2011 values) from January 2003 to December 2011. Sugarcane, sugar, and ethanol prices in São Paulo State.
[b] Tonne of stalk; total reducing sugars content in sugarcane is 15.3%.
[c] Values provided by specialists of the sugarcane industry (15 wt.% moisture content).
[d] Estimate based on Humbird (2011).
[e] Novozymes (2009).
[f] Anhydrous ethanol prices paid to the producer (CEPEA, 2011).
[g] CEPEA (2011).
[h] Average prices obtained at renewable energy auctions in Brazil (2011 values).
[i] MDIC (2011).
[j] Priced based on its energy content and the quotation of anhydrous ethanol.
[k] MDIC (2011).

3. Results and discussion

Important technical parameters obtained from the simulation of each biorefinery scenario, including biomass utilization breakdown (cogeneration and ethanol production), products output, steam and power consumption, and wastewater footprint, are shown in Table 5 and discussed next.

In the BIO-G base case scenario the total steam consumption in the biorefinery is 205 MW, which was generated by the combustion of 66% of the total lignocellulosic biomass (bagasse, straw, and unreacted solids from 2G ethanol production) in combination with the produced biogas (2.2 tonnes of CH_4 per hour). The energy content of the produced biogas is equivalent to that of 3.9 dry tonnes per hour of biomass (or 4.2% of the total available bagasse and straw). Additionally, ethanol produced from biomass (162 L per dry tonne of biomass) accounts for 27% of the ethanol produced in the biorefinery. On the other hand, in the competing case (butanol production) the fraction of biomass used for cogeneration increased to 74% of the total biomass in order to accommodate (i) the steam demand by the butanol plant, which corresponds to ∼10% of the total steam consumption of the biorefinery, and (ii) the absence of biogas production. Consequently, 2G ethanol production dropped by ∼20% in the competing case, or ∼8 million L/year, which is equivalent to 6% of the total ethanol production. Therefore, as the amount of biomass available for each biorefinery scenario is the same, steam demands of the butanol plant were met by decreasing the 2G ethanol production. More specifically, the low pressure steam saved in the mutiple effect evaporators in the ethanol plant was the main source of steam for the butanol plant. According to the steam distribution across major sections in each biorefinery scenario (Fig. 3), whereas in the base case 33% of the steam was mainly used for the concentration of the fermentation broth (sugarcane juice + hydrolyzed liquor + molasses) consumed in the ethanol plant, this percentage decreased to 25% in the competing case because less biomass hydrolyzate was produced.

It is important to note that in the present biorefinery design, lignin (25 wt.% of the biomass in dry basis) is allocated for the cogeneration system in order to boost the production of 2G ethanol. Further studies are necessary to assess the economics of a design in which 2G ethanol production is penalized by driving lignin for the production of high-value precursors to lignin-derived products such as carbon fiber and phenol–formaldehyde (PF) resins. Certainly a phased-approach in this case is strongly recommended in order to minimize market and technical risks. In the first phase of the project, lignin is used for cogeneration while the market(s) for the targeted lignin-derived product(s) is/are developed and technologies for lignin transformation achieve commercial scale.

Table 4
Input parameters for Monte Carlo simulation.

Economic parameter[a]	Distribution function	Most probable[b]	Standard deviation	Min.	Max.
Ethanol price	Normal (3σ)	US$0.66/L	US$0.02/L	–	–
Sugar price	Normal (3σ)	US$0.48/kg	US$0.04/kg	–	–
Sugarcane price	Normal (3σ)	US$27.26/tonne	US$0.45/tonne	–	–
n-Butanol (chemical) price	Normal (3σ)	US$1.65/kg	US$0.02/kg	–	–
n-Butanol (biofuel) price	Normal (3σ)	US$1.03/kg	US$0.02/kg	–	–
Enzyme price[c]	Triangular	US$0.12/L 2G-EtOH	–	−50%	+100%
Power price	Triangular	US$60.98/MWh	–	−10%	+10%
Capital investment in the 1G–2G ethanol–sugar plant (for scenarios with butanol production)	Triangular	377 MUS$	–	−25%	+25%
Capital investment in the 1G–2G ethanol–sugar plant (for scenarios with biogas production)	Triangular	391 MUS$	–	−25%	+25%
Capital investment in the biodigestion unit	Triangular	10 MUS$	–	−25%	+25%
Capital investment in the butanol plant	Triangular	20 MUS$	–	−25%	+25%

[a] Economic parameters with important effect on IRR, according to sensitivity analysis.
[b] For normal distribution, most probable value is the 6-year moving average of prices (December 2011 values) from January 2003 to December 2011.
[c] Price range based on Novozymes (2009).

In the second phase, the corresponding investment on the lignin plant would take place.

Interestingly, the introduction of the butanol plant had no important effect on the amount of power generated, consumed, and the balance sold to the grid. Power is mainly consumed by the series of roller mills that crush the sugarcane, and since the amount of sugarcane processed is the same in both base and competing cases, changes in power consumption were not expected. On the other hand, power generation was unexpectedly the same in both cases. This can be explained due to the fact that the total steam consumption as well as the consumption of each steam level (2.5, 6, 12 bar) were very similar in all cases (Fig. 3). This observation sets the ground for an initial reflexion on the key question raised in the Introduction section, i.e. how much would a reduction in steam consumption in the butanol plant affect power and ethanol production and, consequently, the profitability of the biorefinery? Before answering this question, it is interesting to observe that the combination of the conventional batch fermentation with downstream distillation makes butanol processing significantly more energy-intensive (MJ/kg product) than ethanol processing.

Table 5
Main technical performance parameters of the biorefineries.

Parameter	Scenario		
	BIO-G	RS-C/RS-F	MS-C/MS-F
Lignocellulosic biomass – for cogeneration (dry tonne/h)	34.1	46.9	45.9
Lignocellulosic biomass – for ethanol production (dry tonne/h)	58.3	45.5	46.5
Unreacted solids from 2G ethanol production – for cogeneration (dry tonne/h)	27.1	21.1	21.6
Pentoses liquor (tonne sugars/h)	13.7	10.7	10.9
Pentoses liquor stream (m^3/h)	110.8	86.3	88.3
Ethanol 1G (million L/y)	102.9	102.9	102.9
Ethanol 2G (million L/y)	37.9	29.6	30.2
Total ethanol (million L/y)[a]	140.8	133.4	133.6
Sugar (million tonne/y)	102	102	102
n-Butanol (million L/y)	–	8.8	14.8
Acetone (million L/y)	–	4.5	4.0
Biogas (Nm^3 CH_4/h)	3045	–	–
Power generation (kWh/tonne sugarcane)	124.5	124.5	124.0
Power consumption (kWh/tonne sugarcane)	34.0	34.0	34.0
Power sold to the grid (kWh/tonne sugarcane)	90.5	90.5	90.0
Steam consumption (MW) – biorefinery	205	204	203
Steam consumption (MW) – ethanol plant	151	128	129
Steam consumption (MW) – butanol plant	–	22	20
Specific energy (steam) consumption (MJ/kg ethanol) – ethanol plant	20.8	18.8	18.9
Specific energy (steam) consumption (MJ/kg butanol) – butanol plant	–	44.6	24.0
Energy – as automotive fuel products – generation by biorefinery (MW)[b]	208	212	224
Water consumption for dilution of the pentoses liquor (m^3/h)[c]	–	128	99
Stillage (vinasse) from ethanol plant (m^3/h)	375	353	356
Stillage (vinasse) from biodigestion unit (m^3/h)	103	–	–
L stillage (vinasse)/L ethanol (ethanol plant) [d]	14	11	11
Stillage (vinasse) from butanol plant (m^3/h)	–	214	180
L stillage (vinasse)/L butanol (butanol plant)	–	97	49
Total stillage generation by biorefinery (m^3/h)	478	567	536
Increase in stillage generation due to butanol plant (%)	–	13	11

[a] Includes ethanol produced in the butanol plant (million L/y): 0.91 (RS-C/RS-F) and 0.50 (MS-C/MS-F).
[b] Ethanol plus butanol; respective LHV (MJ/kg): 27.0 and 33.4 (Pfromm et al., 2010).
[c] Values do not include the water stream available from the distillation unit of the butanol plant (10.9 and 14.7 m^3/h, respectively RS and MS), which is also employed for dilution.
[d] Includes stillage from biodigestion unit in scenario BIO-G.

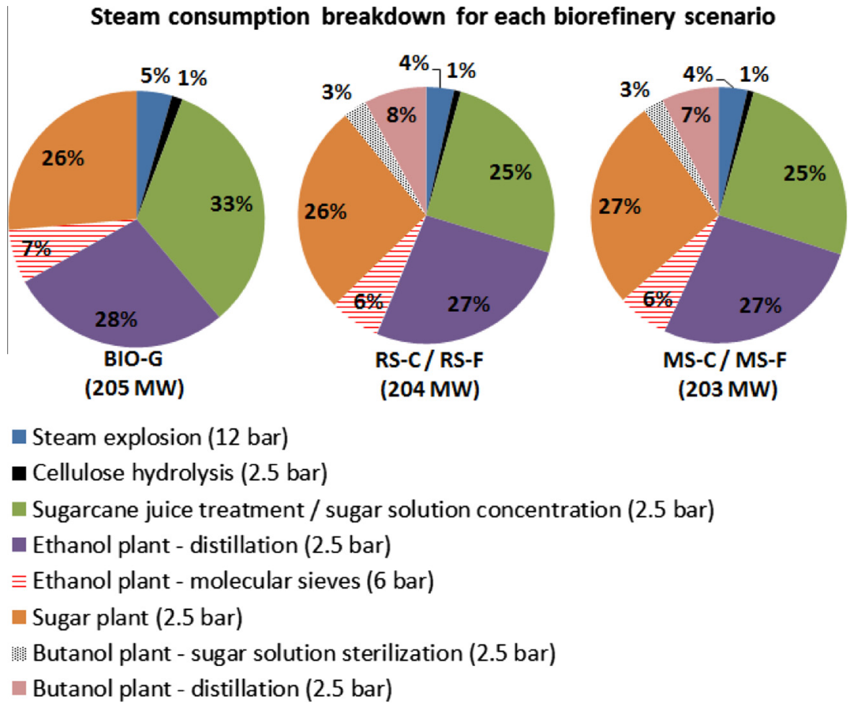

Fig. 3. Steam consumption breakdown for each biorefinery scenario.

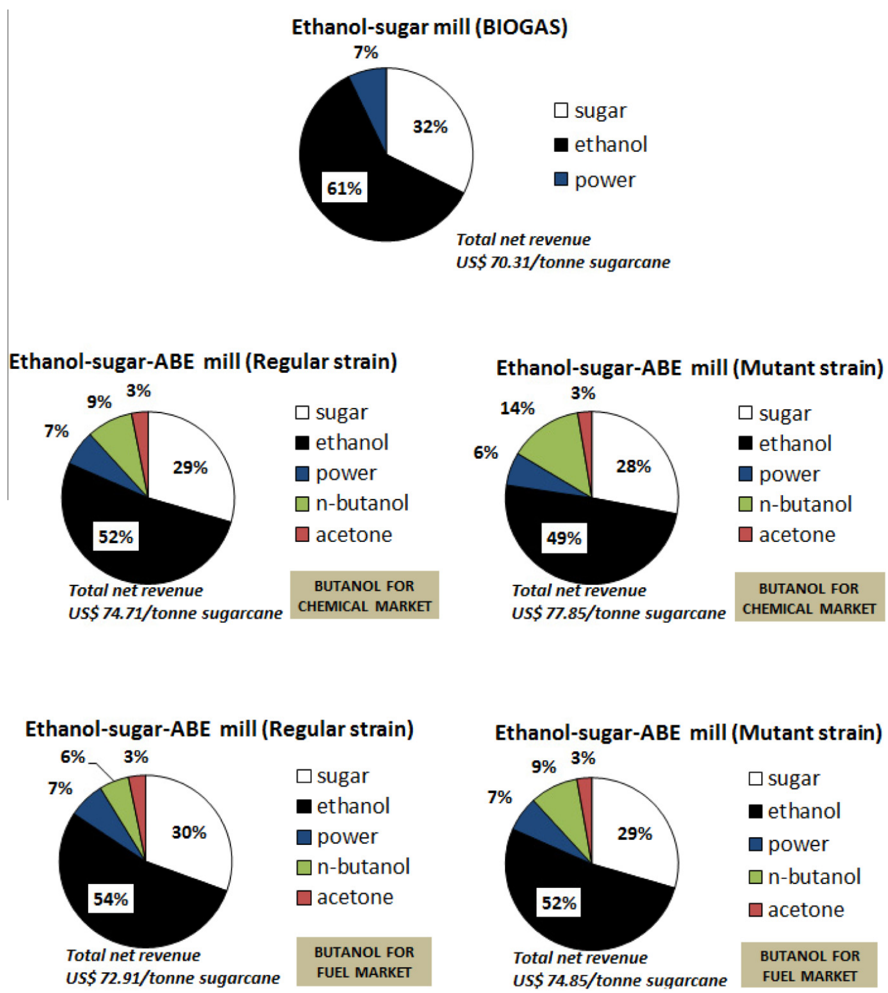

Fig. 4. Revenue breakdown for each biorefinery scenario.

Although the use of a mutant strain with improved butanol yield can result in important reduction of the specific steam consumption, the non-specific steam consumption (MW) barely changes (∼20 MW distributed as 26% for sugar solution sterilization and 74% for distillation) since it is related to the amount of water in the sugar solution processed in the plant and the downstream separation technology. As a result, a good number of research work has been done on the development of fermentation technologies that would allow for fermentation of sugar streams without the need of dilution, such as those that integrate product recovery to the fermentor (Green, 2011; Mariano and Maciel Filho, 2012). Alternatively, or in combination, advanced energy-efficient downstream separation technologies such as liquid–liquid extraction can also bring significant steam saving (Vane, 2008; Kraemer et al., 2011). The effects of reducing steam consumption on the profitability of the biorefinery project are presented following the economic analysis.

Another issue related to fermentation of diluted sugar streams is the high wastewater footprint (L stillage/L product). While in the ethanol plant, fermentors operate with an initial sugar concentration of 160 g/L and final ethanol titer of 80 g/L, in the butanol plant sugar concentration is 50–60 g/L and final butanol titer is 9–17 g/L. As a result, the wastewater footprint in the butanol plant is 4–9 times greater, depending on the Clostridium strain used (regular or mutant). In the case of the fermentation with a regular strain, 97 L of stillage were generated per each liter of butanol produced. This impressive ratio is a critical element that supports the development of hyper-butanol producing strains and advanced fermentation technologies with integrated product recovery. Additionally, as practiced in the past, part of the stillage (25–50%) can potentially be recycled to the system without affecting the fermentation (Walton and Martin, 1979). However, this practice was adopted in mills supplied with cornstarch and molasses and the effects of recycling stillage from fermentations of lignocellulosic feedstocks are still unknown or not publically available. A comprehensive list of fermentation technologies and expected wastewater footprint is presented in Mariano and Maciel Filho (2012).

The scale of the butanol plant was determined by the amount of pentose sugars (11 tonne/h) resulting from the fractionation of 46 dry tonnes per hour of biomass used for the production of 2G ethanol. With this amount of sugar, the plant with a regular strain has a production capacity of 7.1×10^3 tonnes of butanol per year and the fuels production (ethanol + butanol) in the biorefinery increases from 208 MW (base case) to 212 MW (Table 5). The use of a mutant strain with improved butanol yield resulted in an increase in butanol production of 69% or 4.9×10^3 tonnes/year (an increase in gross income of MUS$ 8.1/year – chemical market or MUS$ 5.0/year – fuels market). Although these production capacities can be considered relatively small in comparison to some of the biobutanol plants in China, whose capacities range from 3×10^3 to 100×10^3 tonnes/year (Ni and Sun, 2009), the introduction of butanol and acetone to the product portfolio of the biorefinery increased and diversified its revenues (Fig. 4). Most notably, the revenue contribution from ethanol decreased from 61% to ∼50%, giving room for the new products. This alteration improved the robustness of the biorefinery against expected market fluctuations, considered here through the Monte Carlo risk analysis and robustness measured by the probability of IRR be greater than a target value of 12%. While the base case scenario has an IRR of 11.3% with probability (P) of 0.26 to be greater than 12%, the scenario that considers a microorganism with improved butanol yield and targets the chemical market (MS-C) has an IRR of 15.2% and P equal to 1. Investment and annual costs are presented in Table 6. The other scenarios with butanol production also have a profitability more attractive than the base case, as indicated by the following results: RS-C (13.9% IRR, $P = 0.95$); RS-F (13.1% IRR, $P = 0.80$); and MS-F

Table 6
Investment and annual costs for biorefinery scenarios with processing capacity of two million tonnes of sugarcane per crop season.

Item	Scenario				
	BIO-G	RS-C	RS-B	MS-C	MS-B
Investment costs (MUS$)[1]					
Steam generation system	59	59	59	59	59
Reception-extraction system	28	28	28	28	28
Ethanol plant (1G)	29	29	29	29	29
Ethanol plant (2G)	100	86	86	86	86
Sugar plant	21	21	21	21	21
Butanol plant	–	20	20	20	20
Biodigestion unit	10	–	–	–	–
Turbines/power generators	24	24	24	24	24
Other equipment	21	21	21	21	21
Electromechanical assembly	16	16	16	16	16
Civil works	30	30	30	30	30
Electrical installations	18	18	18	18	18
Instrumentation/automation	5	5	5	5	5
Engineering services, thermal insulation and painting	23	23	23	23	23
Power transmission lines (40 km)	12	12	12	12	12
Heat exchange network	5	5	5	5	5
Working capital	8	8	8	8	8
Total	409	405	405	405	405
Annual costs (MUS$/y)[b]					
Sugarcane	55.1	55.1	55.1	55.1	55.1
Sugarcane straw	3.0	3.0	3.0	3.0	3.0
Enzymes (hydrolysis)	5.5	4.3	4.3	4.3	4.3
Microorganism license (mutant strain)	–	–	–	0.2	0.2
Other inputs	14.9	14.9	14.9	14.9	14.9
Labor	3.5	3.5	3.5	3.5	3.5
Tax over production (0.65%)	1.0	1.0	1.1	1.0	1.0
Income Tax (34%)	10.7	15.0	17.3	12.8	14.1
Total	94	97	99	95	96

[a] US$1.00 = R$ 1.64 (2011 average exchange rate).
[b] First ten years of operation corresponding to the depreciation period.

(13.9% IRR, $P = 0.95$). It is interesting to note that although the selling price of butanol in the automotive fuels market is expected to be significantly lower (~35%) than its current quotation in the chemical market, this alternative is still more attractive than producing biogas and enhance 2G ethanol production. The reader is referred to Mariano et al. (2013) for additional insights into the risks associated with the chemical and fuels markets and with the use of engineered microorganisms.

The sensitivity analysis performed by means of factorial design (Plackett–Burman design) estimated the effects of the economic parameters on the IRR of the biorefinery scenarios. Effects were calculated considering a significance level of 95% and presented in Pareto charts (Fig. 5). A negative effect means that there is a decrease in IRR for every increase in the economic parameter and vice versa. An effect is considered statistically significant if its absolute value is greater than the value indicated by the vertical dotted line in the charts ($P = 0.05$). Due to similarity of results across the scenarios with butanol production, only the scenario MS-C is presented. For the base case scenario (BIO-G), the main economic parameters, in decreasing order of importance, were: ethanol price, sugarcane price, investment cost of the biorefinery without considering the biodigestion unit, and sugar price. Prices of sugarcane straw, power, hydrolytic enzyme, and investment cost of the biodigestion unit have no significant effect on IRR. In the competing case, butanol price has an effect similar to power price, which is now significant. As a result of the revenue diversification, ethanol price is no longer the most important economic parameter and its effect is closer to that of sugarcane price and investment cost of the biorefinery without considering the butanol plant. The investment cost of the butanol plant, acetone price, and microorganism license cost have no significant effect.

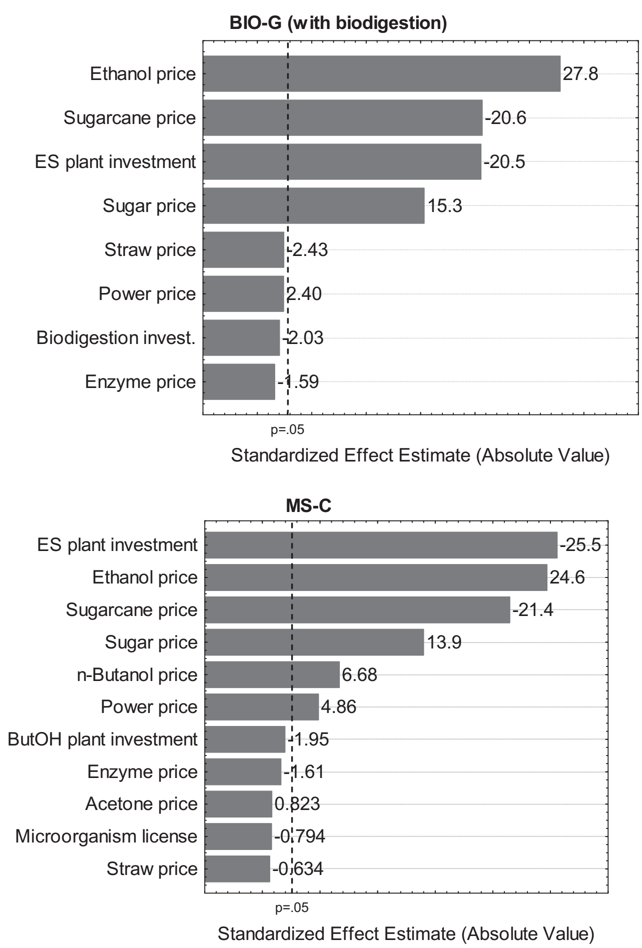

Fig. 5. Sensitivity analysis. Pareto charts of the effects of economic parameters on IRR for biorefinery scenarios BIO-G and MS-C. ES plant stands for the investment in the biorefinery considering neither biodigestion unit nor butanol plant (ButOH plant).

Returning to the question initially discussed during the energy analysis of the biorefinery, it should be firstly noted that the steam consumption in the butanol plant, mostly by the distillation unit, is 1.3 (regular strain) and 0.7 (mutant strain) times the energy (LHV) found in the produced butanol. These numbers are relatively high, especially if compared to the ratio suggested by Vane (2008). According to this author, for an energy-efficient production of biofuels, the energy consumption at the process level should not exceed 1/3 of the energy content of the product. Should this ratio be attained in scenario RS-C, the steam consumption in the butanol plant would decrease from 22 to 5.5 MW. Since the steam consumption in the biorefinery determines the amount of biomass available for 2G ethanol production and, consequently, the amount of C5 sugars available for the butanol plant, for each MW saved the annual income of the biorefinery would increase by MUS$ 0.308, with the following breakdown: 0.170 – ethanol; (−)0.054 – power; 0.142 – butanol; 0.050 – acetone. Thus, for a saving of 16.6 MW, the increase in income would be MUS$ 5.1/year, which is equivalent to 3% of the income of the biorefinery or 26% of the income of the butanol plant. Furthermore, if no additional capital was required, which is very unlikely, IRR would change from 13.9% to 14.7% (0.045%/MW). In more realistic terms, the capital investment in the butanol plant could increase by up to 23 MUS$ before IRR would start to be lower than the original 13.9%.

A reduction of 50–75% in steam consumption can potentially be achieved through the combination of heat integration projects with advanced fermentation and energy-efficient downstream technologies. However, besides the inherent risk related to the scale-up of new technologies, another important challenge in adopting advanced technologies is the fact that the bioethanol industry and equipment suppliers heavily rely on the design and operability of conventional fermentors in combination with downstream distillation. In addition to this paradigm, the risk of entering to a value chain different from that of the ethanol and sugar businesses is no less important. Therefore, the adoption of risk mitigation strategies is crucial to the expansion of the product portfolio of sugarcane biorefineries and to turn the production of chemicals from pentose sugars more attractive than the biogas option, which has minimum technology risk and no market risk, since biogas replaces part of the biomass used for cogeneration. Efficient risk mitigation strategies may include the project execution with an EPC (engineering, procurement, and construction) contract and negotiation of off-take agreements to secure sales.

In the competition between biogas and butanol production proposed in this work, butanol and the by-product acetone are ultimately competing against ethanol. The economic studies presented here demonstrate that the choice for butanol is more profitable, even considering the lower margins of the automotive fuels market and the use of non-engineered microorganisms. Furthermore, in the sugarcane biorefinery context in Brazil, butanol production from a pentose stream resulting from the fractionation of bagasse and sugarcane straw can be considered a better option than the production from the sugarcane juice. In a previous study, Mariano et al. (2013) reported that the investment on a biorefinery that uses 25%, 50%, and 25% of the sugarcane juice to produce, respectively, sugar, ethanol, and butanol, is more attractive than a 50:50 (ethanol:sugar) annexed plant only in the case butanol is produced by an improved microorganism and traded as a chemical. The use of sugarcane juice for butanol production can be considered a straight competition against sugar production, and this is a tough competition since the bull market in sugar prices in the last five years has prompted producers to maximize sugar production (Cavalett et al., 2012). Nevertheless, independently of the sugar source, the production of butanol or other chemicals in sugarcane biorefineries certainly will expand the use of sugarcane. The techno-economic studies of these options are not only useful for the identification and contextualization of technology bottlenecks, but also for supporting decision makers of an industrial sector that has experienced an annual growth rate of 5% in the last 20 years, and according to this growth rate, 140 new greenfield projects are expected to be implemented over the next decade (Fernando Landgraf, IPT, personal communication).

4. Conclusions

In the competition butanol versus biogas, the choice for butanol is more profitable even considering the lower margins of the automotive fuels market and the use of non-engineered microorganisms. The introduction of butanol and acetone to the product portfolio of the biorefinery led to increased and diversified revenues. Although a reduction of steam consumption in the butanol plant decreases the amount of excess power generated in the biorefinery, the return on each MW saved is attractive owing to an increase in the amount of biomass available for ethanol production and, consequently, the amount of sugar available for the butanol plant.

Acknowledgements

We thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support (Contract grant number 2007/00341-1 under the BIOEN Thematic project "An Integrated Process for Total Bioethanol Production and Zero CO_2 Emission", Grant No. 08/57873-8).

References

Afschar, A.S., Vaz Rossell, C.E., Schaller, K., 1990. Bacterial conversion of molasses to acetone and butanol. Appl. Microbiol. Biotechnol. 34, 168–171.
Cavalett, O., Junqueira, T.L., Dias, M.O.S., Jesus, C.D.F., Mantelatto, P.E., Cunha, M.P., Franco, H.C.J., Cardoso, T.F., Maciel Filho, R., Rossell, C.E.V., Bonomi, A., 2012. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. Clean Technol. Environ. Policy 14, 399–410.
CEPEA – Center for Advanced Studies on Applied Economics, 2011. <http://www.cepea.esalq.usp.br> (retrieved 03.12.2011).
Chandel, A.K., Chandrasekhar, G., Radhika, K., Ravinder, R., Ravindra, P., 2011. Bioconversion of pentose sugars into ethanol: a review and future directions. Biotechnol. Mol. Biol. Rev. 6, 8–20.
CTBE – Brazilian Bioethanol Science and Technology Laboratory, 2012. The Virtual Sugarcane Biorefinery (VSB). Technical Report 2012.
Dias, M.O.S., Cunha, M.P., Jesus, C.D.F., Rocha, G.J.M., Pradella, J.G.C., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2011a. Second generation ethanol in Brazil: can it compete with electricity production? Bioresour. Technol. 102, 8964–8997.
Dias, M.O.S., Cunha, M.P., Maciel Filho, R., Bonomi, A., Jesus, C.D.F., Rossell, C.E.V., 2011b. Simulation of integrated first and second generation bioethanol production from sugarcane: comparison between different biomass pretreatment methods. J. Ind. Microbiol. Biotechnol. 38, 955–966.
Dias, M.O.S., Junqueira, T.L., Jesus, C.D.F., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2012. Improving second generation ethanol production through optimization of first generation production process from sugarcane. Energy 43, 246–252.
Ensinas, A.V., Nebra, S.A., Lozano, M.A., Serra, L.M., 2007. Analysis of process steam demand reduction and electricity generation in sugar and ethanol production from sugarcane. Energy Convers. Manag. 48, 2978–2987.
Ezeji, T., Qureshi, N., Blaschek, H.P., 2007. Butanol production from agricultural residues: impact of degradation products on *Clostridium beijerinckii* growth and butanol fermentation. Biotechnol. Bioeng. 97, 1460–1469.
Ezeji, T., Blaschek, H.P., 2008. Fermentation of dried distillers' grains and soluble (DDGS) hydrolysates to solvents and value-added products by solventogenic clostridia. Bioresour. Technol. 99, 5232–5242.
Green, E.M., 2011. Fermentative production of butanol – the industrial perspective. Curr. Opin. Biotechnol. 22, 1–7.
Humbird, D. et al., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol – Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. Report No. NREL/TP-5100-47764, 2011.
Kraemer, K., Harwardt, A., Bronneberg, R., Marquardt, W., 2011. Separation of butanol from acetone–butanol–ethanol fermentation by a hybrid extraction–distillation process. Comp. Chem. Eng. 35, 949–963.
Leibbrandt, N.H., Knoetze, J.H., Görgens, J.F., 2011. Comparing biological and thermochemical processing of sugarcane bagasse: an energy balance perspective. Biomass Bioenergy 35, 2117–2126.
Liu, Z., Ying, Y., Li, F., Ma, C., Xu, P., 2010. Butanol production by *Clostridium beijerinckii* ATCC 55025 from wheat bran. J. Ind. Microbiol. Biotechnol. 37, 495–501.
Macedo, I.C., Seabra, J.E.A., Silva, J.E.A.R., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and a prediction for 2020. Biomass Bioenergy 32, 582–595.
Mariano, A.P., Keshtkar, M.J., Atala, D.I.P., Maugeri Filho, F., Wolf Maciel, M.R., Maciel Filho, R., Stuart, P., 2011. Energy requirements for butanol recovery using the flash fermentation technology. Energy Fuel 25, 2347–2355.
Mariano, A.P., Maciel Filho, R., 2012. Improvements in biobutanol fermentation and their impacts on distillation energy consumption and wastewater generation. Bioenerg. Res. 5, 504–514.
Mariano, A.P., Dias, M.O.S., Junqueira, T.L., Cunha, M.P., Bonomi, A., Maciel Filho, R., 2013. Butanol production in a first-generation Brazilian sugarcane biorefinery: technical aspects and economics of greenfield projects. Bioresour. Technol. 135, 316–323.
Martín, C., Galbe, M., Nilvebrant, N.-O., Jönsson, L.J., 2002. Comparison of the fermentability of enzymatic hydrolyzates of sugarcane bagasse pretreated by steam explosion using different impregnating agents. Appl. Biochem. Biotechnol. 98–100, 699–716.
Mascal, M., 2012. Chemicals from biobutanol: technologies and markets. Biofuel. Bioprod. Biorefin. 6, 483–493.
Marchal, R., Ropars, M., Vandecasteele, J.P., 1986. Conversion into acetone and butanol of lignocellulosic substrates pretreated by steam explosion. Biotechnol. Lett. 8, 365–370.
MDIC, 2011. System Information Analysis of Foreign Trade – Butanol and Acetone Prices. <http://aliceweb.desenvolvimento.gov.br> (retrieved 12.07.2011).
Ni, Y., Sun, Z., 2009. Recent progress on industrial fermentative production of acetone–butanol–ethanol by *Clostridium acetobutylicum* in China. Appl. Microbiol. Biotechnol. 83, 415–423.
Novozymes, 2009. Enabling cost efficient enzymatic hydrolysis for biomass-to-ethanol conversion. In: 7th Global Clean Technology Conference, New York, USA.
Ojeda, K., Ávila, O., Suárez, J., Kafarov, V., 2011. Evaluation of technological alternatives for process integration of sugarcane bagasse for sustainable biofuels production – Part 1. Chem. Eng. Res. Des. 89, 270–279.
Pfromm, P.H., Amanor-Boadu, V., Nelson, R., Vadlani, P., Madl, R., 2010. Bio-butanol vs. bio-ethanol: a technical and economic assessment for corn and switchgrass fermented by yeast or *Clostridium acetobutylicum*. Biomass Bioenergy 34, 515–524.
Qureshi, N., Saha, B.C., Hector, R.E., Dien, B., Hughes, S., Liu, S., Iten, L., Bowman, M.J., Sarath, G., Cotta, M.A., 2010. Production of butanol (a biofuel) from agricultural residues: Part II – use of corn stover and switchgrass hydrolysates. Biomass Bioenergy 34, 566–571.
Rabelo, S.C., Carrere, H., Maciel Filho, R., Costa, A.C., 2011. Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept. Bioresour. Technol. 102, 7887–7895.
Roffler, S., Blanch, H.W., Wilke, C.R., 1987. Extractive fermentation of acetone and butanol: process design and economic evaluation. Biotechnol. Prog. 3, 131–140.
Vane, L.M., 2008. Separation technologies for the recovery and dehydration of alcohols from fermentation broths. Biofuel. Bioprod. Biorefin. 2, 553–588.
Walton, M.T., Martin, J.L., 1979. Production of butanol-acetone by fermentation. In: Pepple, H.J., Perlman, D. (eds.), Microbial Technology, second ed., vol. 1. New York: Academic, pp.187–209.
Wayman, M., Yu, S., 1985. Acetone–butanol fermentation of xylose and sugar mixtures. Biotechnol. Lett. 7, 255–260.
Yu, E.K.C., Deschatelets, L., Saddler, J.N., 1984. The bioconversion of wood hydrolyzates to butanol and butanediol. Biotechnol. Lett. 6, 327–332.