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ORIGINAL PAPER

Simulation of integrated first and second generation bioethanol production from sugarcane: comparison between different biomass pretreatment methods

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Abstract Sugarcane bagasse is used as a fuel in conventional bioethanol production, providing heat and power for the plant; therefore, the amount of surplus bagasse available for use as raw material for second generation bioethanol production is related to the energy consumption of the bioethanol production process. Pentoses and lignin, byproducts of the second generation bioethanol production process, may be used as fuels, increasing the amount of surplus bagasse. In this work, simulations of the integrated bioethanol production process from sugarcane, surplus bagasse and trash were carried out. Selected pre-treatment methods followed, or not, by a delignification step were evaluated. The amount of lignocellulosic materials available for hydrolysis in each configuration was calculated assuming that 50% of sugarcane trash is recovered from the field. An economic risk analysis was carried out; the best results for the integrated first and second generation ethanol production process were obtained for steam explosion pretreatment, high solids loading for hydrolysis and 24–48 h hydrolysis. The second generation ethanol production process must be improved (e.g., decreasing required investment, improving yields and developing pentose fermentation to ethanol) in order for the integrated process to be more economically competitive.

Keywords Simulation · Sugarcane · Sugarcane bagasse · Ethanol · Pretreatment · Enzymatic hydrolysis

Introduction

Bioethanol has been produced from sugarcane in Brazil on a large scale for more than 30 years [14]. Until 2005, Brazil was the largest ethanol producer in the world, but international interest in ethanol as a fuel aroused and motivated an increase of ethanol production from corn in the USA. Nevertheless, sugarcane remains the most efficient raw material for bioethanol production, with lower consumption of fossil energy for ethanol production, producing an average of 9.3 units of renewable energy for one unit of fossil energy consumed [22].

In the search for the expansion of bioethanol production without compromising food security and assuring fuel supplies, the use of lignocellulosic materials such as surplus bagasse, trash and other agricultural residues has been encouraged; it is estimated that the use of these raw materials for bioethanol production will improve process efficiency as well as reduce environmental impacts [23, 37]. Bioethanol production from lignocellulosic materials (second generation (2G) bioethanol), including pretreatment processes and enzymes technology for cellulose saccharification, has been investigated with increasing interest for the past few years [36], due to the growing concerns about climate change, increased energy demand and the forecast depletion of fossil resources [10, 32].

One of the major lignocellulosic materials that can be employed for bioethanol production is sugarcane bagasse,

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the fibrous lignocellulosic residue generated in large amounts (approximately 140 kg/ton of sugarcane, dry basis) during sugarcane processing for sugar and ethanol production [20]. Where bioethanol is produced from sugarcane (first generation (1G)), such as in Brazil, sugarcane bagasse is already available at plant sites, and production of second generation bioethanol can share part of the infrastructure where first generation bioethanol is produced, such as juice concentration, fermentation and distillation [7], and the utilities sector (cogeneration and water cooling systems). Another important residue that may be employed for bioethanol production in the sugarcane industry is sugarcane trash, which includes sugarcane leaves and tops, usually burnt or left in the field; trash is produced at a rate of approximately 140 kg/ton of sugarcane (dry basis). With the elimination of burning practices, large amounts of trash will be available for use as an energy source [34].

Since sugarcane bagasse is used as a fuel in conventional bioethanol production, providing heat and power for the plant [11], the amount of surplus bagasse available for use as raw material for second generation bioethanol production is directly related to the energy consumption of bioethanol production processes (both first and second generation). Pentose and lignin, byproducts of the second generation bioethanol production, may be used as fuels [21] to increase the amount of surplus bagasse, along with improved technologies for cogeneration and optimization of the conventional bioethanol production process [11].

In order to be used as raw materials for bioethanol production, lignocellulosic materials such as sugarcane bagasse and trash must undergo a pretreatment process through which the hemicellulose is removed and the cellulose is made more accessible to enzymatic attack during hydrolysis [28, 31]. Different pretreatment processes have been investigated including physical (comminution), chemical (alkali, acid and solvents attack), physico-chemical (steam explosion) and biological (white-rot fungi attack) approaches [35], but none have yet upgraded second generation to levels of production competitive with conventional first generation ethanol production.

In order to point toward the most adequate configuration of the second generation ethanol production process, in a process integrated with conventional first generation from sugarcane, simulations of the integrated bioethanol production process from sugarcane, surplus bagasse and trash were carried out using the SuperPro Designer process simulator [17]. Selected pre-treatment methods (steam explosion, hydrogen peroxide and organosolv) followed, or not, by an alkaline delignification step were evaluated, along with the subsequent enzymatic hydrolysis step. The amount of lignocellulosic material available for hydrolysis on each configuration was calculated assuming that 50% of sugarcane trash is recovered from the field [7, 39] and used either as fuel in the cogeneration system or as raw material for bioethanol production, if the thermal requirements of the plant are low enough, resulting in surplus trash. Yields, process and conversion parameters were obtained in the literature and from the industry for the first generation process, and bioethanol production was evaluated for each process configuration.

This work provides a basis for economic evaluations to determine the feasibility of integrated second generation bioethanol production.

Process description

Sugarcane is comprised of sugars (mainly sucrose and small fractions of the reducing sugars fructose and glucose), water, fibers and impurities. Sugarcane composition varies greatly among varieties, climate, soil and age. It is expected that over the next few years sugarcane quality will be enhanced, with an increase in its sugars and fiber content [22]; thus, an improvement in these parameters is considered in this work, in comparison with present sugarcane quality in Brazil.

In this work an autonomous distillery is considered, that is, a plant in which all the processed sugarcane is diverted for ethanol production. A typical large scale plant (crushing around 12,000 tons of sugarcane—TC per day) is simulated. The main parameters of the plant are displayed in Table 1.

First generation bioethanol production from sugarcane

The conventional bioethanol production process in an autonomous distillery follows these main steps: sugarcane reception and cleaning, extraction of sugars, juice treatment and concentration, fermentation, distillation and dehydration.

Upon reception in the factory, sugarcane must be cleaned to remove part of the dirt carried along from the

Table 1 Plant design: main parameters

Parameter	Value	Unit
Sugarcane crushing rate	500	TC/h
Days of operation	180	days/year
Fiber content	14	wt%
Sugars content	15	wt%
Amount of sugarcane trash produced in the field	140	kg/TC
Fraction of sugarcane trash recovered from the field	50	%

TC tons of sugarcane

field. Sugarcane cleaning is usually carried out using wash water, which is recycled to the cleaning process after removal of dirt and other impurities.

Extraction of sugars is done using mills, where sugarcane juice and bagasse are separated. Water at a rate of 28 wt% of sugarcane flow is used to improve sugars recovery. Sugarcane juice contains water, sucrose and reducing sugars, along with impurities such as minerals, salts, organic acids, dirt and fiber particles which must be removed prior to fermentation. First, screens are used to remove sand and fine particles of bagasse [5]. Juice then receives a chemical treatment to remove other impurities. In the process considered in this work, juice undergoes heating from 30 to 70°C; addition of lime takes place afterwards along with a second heating, up to 105°C. Hot juice is flashed to remove dissolved air and, after addition of a flocculant polymer, impurities are removed in a settler, where mud and clarified juice are obtained. A filter is used to recover some of the sugars carried along with the mud, and the filtrate is recycled to the process prior to the second heating operation.

Clarified juice contains around 15 wt% solids; a fraction of the clarified juice is concentrated in a 5-stage multiple effect evaporators (MEE) up to 65 wt% solids. The concentrated juice is mixed with the remaining clarified fraction to produce a final juice containing 22.5 wt% solids which is cooled and fed to the fermentors.

A fed-batch fermentation process with cell recycling (Melle-Boinot process) is used [33]. In this process, yeast (recovered from a previous fermentation batch) is fed to the fermentor prior to the juice; the mixture remains in the reactor for a few hours, and the sugars (sucrose, glucose and fructose) are converted into ethanol, carbon dioxide and by-products (alcohols, organic acids, etc.). Since fermentation reactions are exothermic, fermentation vats are cooled in order to attain high ethanol concentration in the fermented liquor (also called wine) [9]. The wine produced in fermentation is centrifuged to remove yeast cells, which undergo a chemical treatment using water and sulfuric acid to reduce bacterial contamination. Yeast cells are used in the next batch, while centrifuged wine is purified in distillation and rectification columns, producing hydrous (around 93 wt%) ethanol. Anhydrous ethanol (99.3 wt%) is produced in an adsorption process using molecular sieves.

The main parameters of the unit operations of the bioethanol production process that constitutes an autonomous distillery are represented in Table 2. The efficiencies and other parameters displayed in Table 2 represent equipment commercially available in Brazil.

Table 2 Unit operation design: main parameters

Parameter	Value	Unit
Efficiency of dirt removal on sugarcane cleaning	90	%
Sugar losses on sugarcane cleaning	0.8	kg/TC
Sugarcane wash water	2.2	m^3/TC
Efficiency of sugars extraction on the mills	97.5	%
Sugarcane bagasse moisture content	50	wt%
Recovery of sugars on juice treatment	99.5	%
Fermentation yield	92	%
Ethanol recovery on distillation and dehydration	99.7	%
Pressure of steam produced in the boilers	90	bar

TC tons of sugarcane

Second generation bioethanol production processes

Second generation biofuels are produced from lignocellulosic biomass, which is basically composed of three polymers: cellulose, hemicelluloses (mainly xylan) and lignin [1]. While the hemicellulosic fraction is converted into monomeric sugars (mainly pentoses) under mild process conditions, hydrolysis of cellulose into glucose, which is easily fermented to ethanol, is considerably harder to accomplish [30].

Due to the close association of the three components (cellulose, hemicellulose and lignin) in the structure of the biomass, an intense pretreatment process is required to separate lignin and hemicellulose from the cellulose by promoting their solubilization or degradation, reducing cellulose crystallinity and increasing porosity of the lignocellulosic material, thus improving accessibility of the remaining cellulose to enzymatic attack [19, 26, 31].

The process of production of bioethanol from lignocellulosic materials consists of the following operations: biomass pretreatment, hydrolysis, concentration, fermentation, separation, purification and effluent treatment and disposal [36].

In Brazil, sugarcane bagasse is an important raw material to be considered for ethanol production, via hydrolysis, due to its low costs and the possibility of sharing infrastructure in existing mills, thus reducing required investments [39]. In addition, another lignocellulosic residue obtained from sugarcane—sugarcane trash—may be recovered from the fields and used as raw material for second generation bioethanol production. However, a fraction of the trash produced must be left in the field in order to provide weed and disease control as well as soil conservation and fertilizer recycling. The exact amount of trash that must be left in the field depends on local conditions such as variety, climate, pests and others [15], but several authors consider that the use of 50% of the trash in the mills is a feasible figure in the years to come [7, 39].

In this work, different pretreatment methods were considered and compared: steam explosion, hydrogen peroxide and organosolv, followed, or not, by an alkaline delignification step.

SO_2 catalyzed steam explosion

Experimental results of the steam pretreatment process of sugarcane bagasse and the subsequent enzymatic hydrolysis were obtained by Carrasco et al. [3]. The authors performed a series of experiments in which 300 g of bagasse (dry weight) was steam pretreated in a 10 L steam-pretreatment reactor, using SO_2 as a catalyst, followed by enzymatic hydrolysis (1 L reactors) and fermentation.

The highest values for soluble xylose recovery were obtained for SO_2 catalyzed steam pretreatment at 190°C for 5 min, which also provided the highest overall sugar yields (including monosaccharides produced upon pretreatment and hydrolysis) after enzymatic hydrolysis [3].

Alkaline hydrogen peroxide

Alkaline processes are expected to cause less sugar degradation than acid processes; since hydrogen peroxide degrades into water and oxygen, it does not contaminate biomass. Another advantage of this process is the fact that it takes place under mild process conditions (pressure, temperature and no acid catalysts) [28]. In this work, we used results obtained by Garcia [13] for the enzymatic hydrolysis of hydrogen peroxide pretreated bagasse at a solids content of 5%. The optimum pretreatment conditions were defined as 1 h of reaction, 25°C, 11% H_2O_2, pH = 11.5 and 8% bagasse (wt/v). The subsequent enzymatic hydrolysis step was carried out for up to 72 h [13].

Organosolv pretreatment

Sugarcane bagasse was submitted to ethanol organosolv pretreatment using a 50 L pilot scale reactor [24], in which an aqueous ethanol solution (50% v/v) and a solid to liquid ratio of 1:5 were employed, at a constant temperature of 175°C. Different concentrations of catalysts were evaluated, with varying pretreatment times. The subsequent enzymatic hydrolysis step was performed on the washed water-insoluble residue of pretreated bagasse at 5% (w/v) substrate content on a laboratory scale (25 mL) for up to 24 h. The best pretreatment results in terms of overall glucose yield (20.9 g glucose/100 g bagasse) were obtained using 1.25% H_2SO_4 as catalyst for 60 min [24].

Alkaline delignification

Alkali pretreatment decreases both lignin and hemicellulose content of the biomass; combination of dilute NaOH pretreatment and other treatments seems more efficient than the exclusive use of alkali pretreatment [1]. Removal of lignin from the pretreated material improves cellulose accessibility to enzymes in the hydrolysis step.

Cogeneration: co-production of heat and power

Fibrous sugarcane residues (bagasse produced in the mills and trash recovered from the fields) are used as fuels for production of steam and electric energy in the cogeneration system, supplying the entire thermal and electrical requirements of the ethanol production process.

In the production of first generation bioethanol, all the bagasse and trash available are used as fuel in boilers, producing high pressure steam. Steam is fed to extraction-condensation steam turbines, in which low pressure steam is produced to supply the thermal requirements of the process as well as electrical energy, while surplus steam is condensed. When second generation bioethanol is produced, surplus bagasse and trash are used as raw materials in the pretreatment and hydrolysis processes, and in this case the process determines the amount of steam that is produced in the boilers; thus, back-pressure steam turbines (no condensation) are employed [11]. A simplified scheme of the cogeneration systems for first and second generation bioethanol production is illustrated in Fig. 1.

When second generation bioethanol production is integrated with the first generation, the exact amount of lignocellulosic material available for hydrolysis is determined according to the thermal requirements of the entire process, since a portion of the material available must be burnt in the boilers to supply the energy requirements of the integrated plant. Thus, lower energy demand of the production process leads to higher amounts of bagasse and trash available for hydrolysis. One of the tools that can be employed to reduce the thermal energy requirements of the process is the Pinch Analysis [7], through which thermal integration of the process streams is evaluated. Different authors applied this method to analyze the thermal integration of the bioethanol production process [7, 8, 11, 12, 16, 27], promoting a significant reduction in steam consumption of the process.

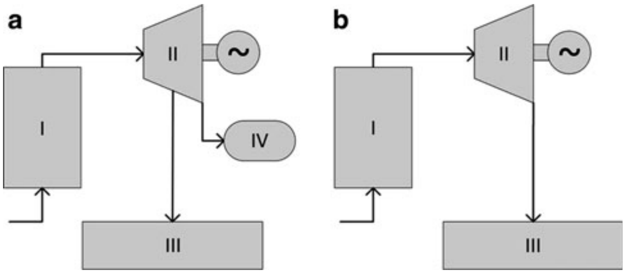


Fig. 1 Simplified scheme of the cogeneration system for the first (**a**) and second (**b**) generation bioethanol production. I: boiler; II: steam turbines; III: process; IV: condenser

Process simulation

Simulations were carried out using the SuperPro Designer process simulator from Intelligen, Inc. An autonomous distillery with modern commercial technologies was considered for the first generation bioethanol production. A simplified scheme of the simulation of the first generation ethanol production is displayed in Fig. 2.

In order to represent the process more accurately, several components that are part of sugarcane composition (cellulose, hemicellulose, lignin, aconitic acid, which represents the acids present in sugarcane structure, and potassium oxide, which represents all the minerals), material dragged along with sugarcane (dirt), by-products (such as aconitate, formed during juice treatment, and pentoses produced during pretreatment and hydrolysis reactions in the simulation of the second generation process) and input material (flocculant polymer, used on juice treatment in the settler) were inserted into the simulator database.

First, a mass balance of the first generation process was carried out using an electronic spreadsheet, using data collected in the industry (Usina da Pedra, a mill producing sugar and ethanol located in the state of São Paulo) and from the literature; the main parameters are the ones reported in Table 2. Simulation of the production process was carried out using SuperPro Designer; the current version of this software (v. 7.5) does not allow the simulation of the cogeneration system, which was calculated using a spreadsheet and integrated with the SuperPro simulation. The parameters adopted for the simulation of the cogeneration system are listed in Table 3.

Simulation was performed considering no thermal integration of process streams. However, a reduction of 30.8% on the 2.5 bar steam consumption calculated by the process simulator was taken into account; this reduction was obtained after applying Pinch Analysis on the simulation of an autonomous distillery by Dias et al. [8].

Simulation of the second generation production process was carried out considering conversion parameters calculated from the results published in Carrasco et al. [3] for the steam explosion (SE), Garcia [13] for the hydrogen peroxide (H_2O_2) and Mesa et al. [24] for the organosolv pretreatment (OS). The main parameters for the 2G processes analyzed are presented in Table 4.

The values presented in Table 4 were obtained for the hydrolysis of sugarcane bagasse at a solid load of 5%; these figures were used in the simulations. An advanced hydrolysis scenario was also considered for each studied pretreatment process, in which enzymatic hydrolysis is carried out at a solids load of 15%, assuming that the same hydrolysis yields illustrated in Table 4 are achieved. In addition, alkaline delignification of pretreated bagasse for both steam explosion and hydrogen peroxide pretreatments was considered; in this case, a hypothetical increase of 20% on the hydrolysis yields displayed in Table 4 was assumed.

The integrated 1G and 2G production process considers fermentation of mixed sugarcane juice and hydrolyzed glucose liquor; a block-flow diagram of the integrated process is shown in Fig. 3.

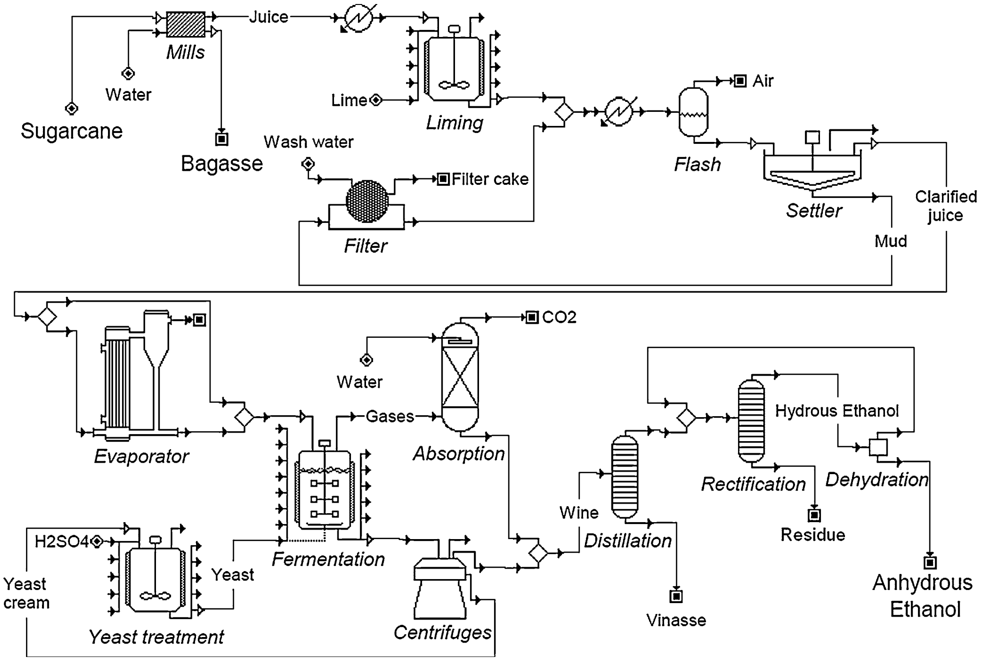


Fig. 2 Simplified scheme of the simulation of the first generation ethanol production from sugarcane in an autonomous distillery

Table 3 Cogeneration design: main parameters

Parameter	Value	Unit
Boiler pressure	90	bar
Boiler efficiency—LHV basis	86	%
Live steam temperature	520	°C
Isentropic efficiency—first stage of steam turbine	72	%
First extraction—steam pressure	22	bar
Isentropic efficiency—second stage of steam turbine	81	%
Generator efficiency	98	%
Isentropic efficiency—condensing turbine	70	%
Condensation pressure	0.11	bar
LHV sugarcane bagasse—50% moisture	7565	kJ/kg
Electricity demand—1G production process	30	kWh/TC
Electricity demand—2G production process	24	kWh/t[a]
LHV sugarcane trash—15% moisture	12960	kJ/kg
LHV biogas	21320	kJ/Nm^3
Process steam pressure	2.5	bar
Molecular sieves—steam pressure	6	bar
Steam explosion pretreatment—steam pressure	12.5	bar
Organosolv pretreatment—steam pressure	10	bar

TC tons of sugarcane

[a] Electricity demand as a function of the lignocellulosic material processed in the second generation production process

Table 4 Second generation pretreatment process design: steam explosion (SE), hydrogen peroxide (H_2O_2) and organosolv (OS): main parameters

Parameter	SE	H2O2	OS
Conversion of xylan during pretreatment (%)	57	67	57
Conversion of cellulose during pretreatment (%)	5	0.7	0
Conversion of cellulose—24 h hydrolysis (%)	50	61	38
Conversion of cellulose—48 h hydrolysis (%)	70	70	NA
Conversion of cellulose—72 h hydrolysis (%)	72	77	NA
Enzymatic load—cellulase (FPU/g dry biomass)	15	10	15
Enzymatic load—β-glucosidase (IU/g dry biomass)	24	20	15

NA data not available

The 2G bioethanol production in this work considered exclusively the fermentation of the glucose obtained from cellulose hydrolysis; the pentose fraction, obtained from the hemicellulose, is biodigested, producing biogas which is used as a fuel. Cellulignin, another by-product of the 2G production, which comprises the remaining solid material after hydrolysis, is also used as fuel in boilers, besides the lignin obtained after alkaline delignification. The use of the process by-products (pentose, lignin and unreacted cellulose) as fuels allows processing of larger fractions of bagasse, since they supply part of the energy required to run the process.

In order to calculate the energy provided by cellulignin burning, Eq. 1 was employed [6]:

$$\mathrm{HHV} = 0.0877(\mathrm{L}) + 16.4951 \quad (1)$$

in which the higher heating value (HHV, kJ/g) is calculated based on the lignin content of the lignocellulosic material (L, wt%). The value calculated using this correlation presented a difference from the experimental value of less than 2% for materials such as tobacco leaf, corncob, corn straw and wheat straw, among others [6]. Lower heating values (LHV) for unreacted cellulignin (moisture content around 50% and varying composition according to the pretreatment and hydrolysis yields) around 10,000 kJ/kg were obtained.

Economic assumptions and parameters

A preliminary economic risk analysis was carried out, considering the basic parameters displayed in Table 5 and the most relevant costs and prices presented in Table 6.

Investment data for the first generation biorefinery was calculated based on data provided by Dedini (one of the major equipment manufacturers for the ethanol industry in Brazil). Table 7 shows these data for an autonomous distillery crushing 2,000,000 tons of sugarcane per year, operating with 22 bar boilers and with azeotropic distillation as the ethanol dehydration method.

Process improvements considered dehydration with molecular sieves (increase of 40% on the distillation sector), boilers for production of 90 bar steam (increase of 40% on the cogeneration sector) and a heat exchanger network (increase of 10% on the distillation sector).

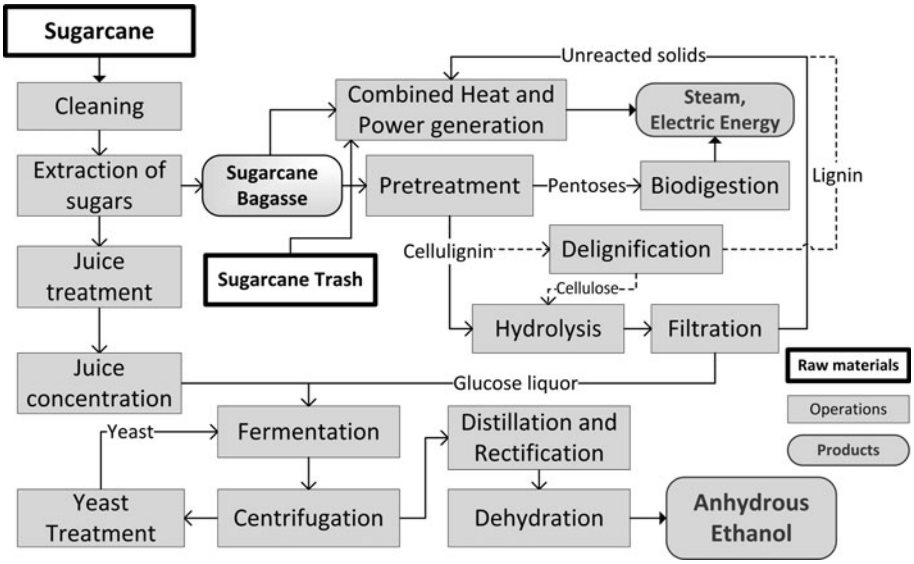


Fig. 3 Block-flow diagram of the integrated 1G and 2G production process

Table 5 Economic analysis: main adopted parameters

Parameter	Value
Project lifetime	25 years
Salvage value of equipment	–
Construction and start-up	2 years
Depreciation (linear)	10 years
Tax rate (income and social contributions)	34.0%

Changes in equipment capacity were correlated to costs considering a coefficient of 0.6.

Investment calculation on the 2G process considered results obtained for equipment dimensions and data available from SuperPro Designer [17], and values for individual equipment available at the "Corn Stover to Ethanol Model" [18].

Results and discussions

Nineteen Alternatives (hereafter named scenarios) were simulated, considering production of 1G and 2G ethanol, different pretreatment methods, such as steam explosion (SE) and hydrogen peroxide (H_2O_2) followed, or not, by an alkaline delignification step (NaOH) and organosolv pretreatments, considering different length of hydrolysis

Table 6 Average costs and prices adopted in the economic risk analysis

Parameter	Lower	Medium	Higher
Overall investment	$x - 3\sigma$	x	$x + 3\sigma$
Sugarcane average cost (US\$/TC)[a]	18.37	19.44	20.50
Sugarcane trash average cost (US\$/t)	10.02	15.02	20.03
Electricity average price (US\$/MWh)[b]	59.09	70.61	82.14
Ethanol average price (US\$/L)[c]	0.46	0.50	0.54
Enzyme average cost (US\$/t)[d]	40.27	118.44	196.61
Hydrogen peroxide average cost (US\$/t)[e]	308.45	462.44	616.44
Sulfur average cost (US\$/t)[e]	43.00	126.46	209.92
Sulfuric acid average cost (US\$/t)[e]	32.24	65.79	99.35
Sodium hydroxide average cost (US\$/t)[e]	104.08	189.24	274.40

[a] 6-year moving average of sugarcane prices (Dec 2009 values) in São Paulo state (SP), from July 2000 to December 2009 [38]

[b] Minimum, medium and maximum prices on renewable energy auctions, values for 2009

[c] 6-year moving average of anhydrous ethanol prices paid to the producer (Dec 2009 values) in SP, from July 2000 to December 2009 [4]

[d] Enzyme prices correspond to approximately between US\$ 0.50 and US\$ 1.25/gal 2G ethanol [25], for a steam explosion pretreatment with 5% solids loading on hydrolysis

[e] Catalyst average prices obtained from Brazilian average import and export prices from 2000 to 2009 [2]; the exchange rate of US\$ 1.00 = R\$ 1.99 was adopted

Table 7 Investment data for an autonomous distillery

Parameter	Value
Overall investment (million US$)	150
Investment on sugarcane reception and juice extraction (%)	15
Investment on juice treatment, fermentation and distillation (%)	17
Investment on the cogeneration system (%)	30
Investment on other sectors (%)	38

(24, 48 and 72 h) and different solids loading on hydrolysis (5 and 15%). The amount of lignocellulosic material available for hydrolysis in each scenario was calculated. The main results are displayed in Table 8.

Ethanol production in the integrated process

It can be verified that for the same hydrolysis conditions, the overall ethanol productions (L/TC liters per ton of sugarcane processed) are very similar for both hydrogen peroxide and steam explosion pretreatments, considering the conversion parameters obtained in the literature (Table 4)—for instance, 108.6 and 107.5 for H_2O_2 and SE pretreatments at 5% solids for 24 h hydrolysis, respectively. In addition, the increase on overall ethanol production obtained when hydrolysis is carried out at a 5% solids load for 72 h is not significant (less than 3%) when compared to that obtained after only 24 h of hydrolysis. The organosolv pretreatment presented the overall lowest ethanol production in the integrated process, due to the fact that it requires a larger amount of energy during pretreatment, leading to lower amounts of surplus lignocellulosic material for 2G ethanol production.

On the other hand, increasing the solids load during hydrolysis leads to a decrease in energy consumption of the process, and so has a significant impact on the amount of lignocellulosic materials available for hydrolysis, thus improving 2G ethanol production.

Equipment size

While installed capacity in pretreatment reactors is a function of the amount of lignocellulosic materials processed and the solids content on the pretreatment operation, hydrolysis reactor sizes also vary tremendously depending on the hydrolysis time (24, 48 or 72 h) and solids loading on hydrolysis (5 or 15%), as can be verified in Fig. 4.

Thus, increasing the time of hydrolysis leads to extremely large hydrolysis reactors (up to 77,000 m^3). As mentioned before, increasing the time of hydrolysis from 24 to 72 h leads to small increments on overall ethanol production: from 2.6% for the hydrogen peroxide (H_2O_2) pretreatment with 5% solids to 6.2% for the steam explosion (SE) pretreatment with 15% solids.

In addition, performing an alkaline delignification step (NaOH) after pretreatment promotes a reduction in the size

Table 8 Overall anhydrous ethanol production, surplus electricity and 2G ethanol production based on the amount of sugarcane (TC—tons of sugarcane) and amount of lignocellulosic materials used as feedstock for second generation ethanol production for each scenario

Scenario	Ethanol production (L/TC)	Surplus electricity (kWh/TC)	Lignocellulosic material processed (t/day, dry basis)	2G ethanol (L/TC)
1G	92.7	173.4	0	0.00
1G + H_2O_2, 5%, 24 h	108.6	98.0	1,311	15.84
1G + H_2O_2, 5%, 48 h	110.3	95.9	1,260	17.58
1G + H_2O_2, 5%, 72 h	111.4	94.5	1,226	18.69
1G + H_2O_2, 15%, 24 h	116.0	62.8	1,923	23.31
1G + H_2O_2, 15%, 48 h	119.0	62.7	1,879	26.29
1G + H_2O_2, 15%, 72 h	120.8	62.4	1,835	28.04
1G + SE, 5%, 24 h	107.5	115.2	1,532	14.74
1G + SE, 5%, 48 h	111.3	108.7	1,396	18.57
1G + SE, 5%, 72 h	111.6	107.9	1,379	18.92
1G + SE, 15%, 24 h	113.5	72.7	2,143	20.73
1G + SE, 15%, 48 h	119.9	71.8	2,033	27.20
1G + SE, 15%, 72 h	120.6	71.6	2,018	27.82
1G + OS, 5%, 24 h	105.4	107.3	766	12.68
1G + OS, 15%, 24 h	110.2	98.5	1,056	17.51
1G + H_2O_2, 5%, 24 h, NaOH	112.4	83.8	1,379	19.67
1G + H_2O_2, 15%, 24 h, NaOH	118.5	59.7	1,805	25.80
1G + SE, 5%, 24 h, NaOH	111.7	97.5	1,685	18.97
1G + SE, 15%, 24 h, NaOH	116.0	68.0	2,055	23.28

1G, first generation ethanol production; H_2O_2, hydrogen peroxide pretreatment; SE, steam explosion; OS, organosolv; NaOH, alkaline delignification after pretreatment; 5 and 15%, solids loading on hydrolysis; 24, 48 and 72 h, hydrolysis length

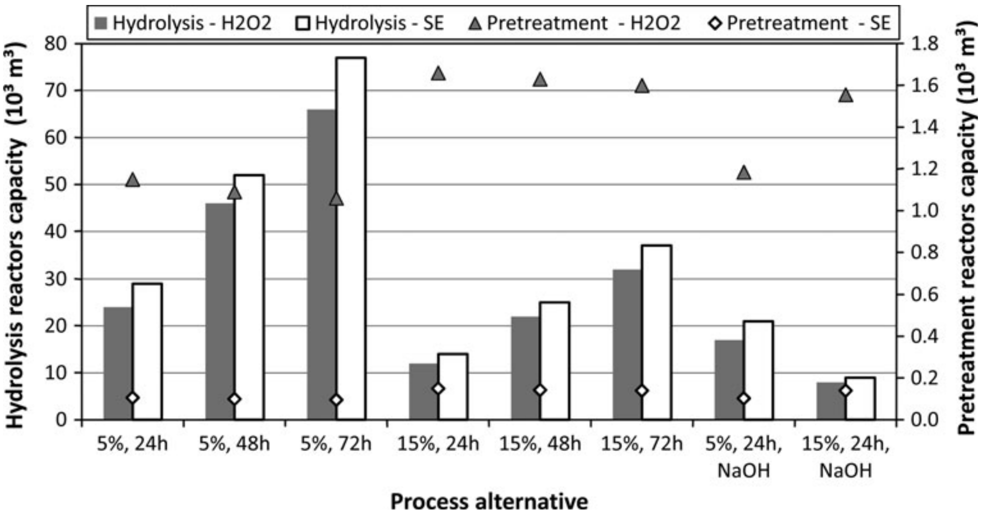


Fig. 4 Installed capacity of hydrolysis and pretreatment reactors for each process alternative

of the hydrolysis reactors, due to the fact that most of the lignin present in the pretreated bagasse (which comprises around 40% of the dry cellulignin) is removed. Consequently, the best configurations for the production of 2G seem to be those that consider 24 h hydrolysis with increased solids load and delignification of the pretreated material.

Input materials and catalysts

Another issue that must be addressed when evaluating 2G ethanol production is the consumption of catalysts and other substances. Due to the fact that the hydrogen peroxide pretreatment takes place in a reactor with 8 wt% solids and 11% peroxide (v/v), enormous amounts of H_2O_2 are required to run the process: from 60 t/h (for the hydrogen peroxide pretreatment with 5% solids and 72 h of hydrolysis) to 95 t/h (15% solids, 24 h hydrolysis) of H_2O_2 (100%); the actual amount employed would be larger, since industrial H_2O_2 is obtained at concentrations up to 70% (v/v). In fact, the amount of hydrogen peroxide consumed in this process is larger than the amount of overall anhydrous ethanol produced, including 1G ethanol. Thus, unless the amount of catalyst is reduced dramatically, this process requires a large industrial plant for hydrogen peroxide production to be placed next to the sugarcane processing plant. Studies considering reduction on catalyst consumption are under development [29].

In the organosolv pretreatment, an aqueous ethanol solution (50% v/v) is employed at a solid to liquid ratio of 1:5; after pretreatment, the mixture is filtered and the liquid fraction is fed to a distillation column, where solvent recovery takes place. In this column, some ethanol loss on the bottom stream occurs, thus decreasing the overall production of ethanol. In addition, the extreme pretreatment conditions (175°C, around 20 bar) involve a large consumption of energy, which reduces the amount of surplus bagasse and trash available for 2G ethanol production when compared to the other pretreatment methods analyzed in this work. Sulfuric acid is used in this process as well.

Sulfur dioxide for the steam explosion pretreatment is produced on site by consuming up to 0.9 t/h of sulfur on combustion chambers. This process is already used in some sugarcane mills, since sulfur dioxide is used as a bleach to reduce color in the sugar production process.

The amount of enzymes required on the hydrolysis step of each process was evaluated based on the values provided in the literature: 10 FPU/g and 10 CBU/g of dry biomass material (DM) for the hydrogen peroxide pretreatment [13], 15 FPU/g and 15 IU/g DM [24] for the organosolv pretreatment and around 15 FPU/g and 24 IU/g DM [3] for the steam explosion pretreatment (these conditions were defined for 5% solids on hydrolysis). The amount of enzymes was estimated considering that the enzymes employed have the following activities, based on values determined by Carrasco et al. [3]: 65 FPU/g for cellulase and 376 IU/g of *β*-glucosidase.

Economic analysis

Results for the overall investment for each alternative are shown in Fig. 5.

A significant increase of investment is required for the integrated process where 2G considers hydrolysis at 5% solids loading and longer hydrolysis times.

An economic risk analysis was carried out in order to evaluate the processes for 2G ethanol production employed in an integrated sugarcane plant. The values depicted in Tables 5 and 6 were employed. An electronic spreadsheet was developed to evaluate the internal rate of return for the different alternatives of integrated 1G and 2G ethanol

Fig. 5 Investment for the process alternatives evaluated

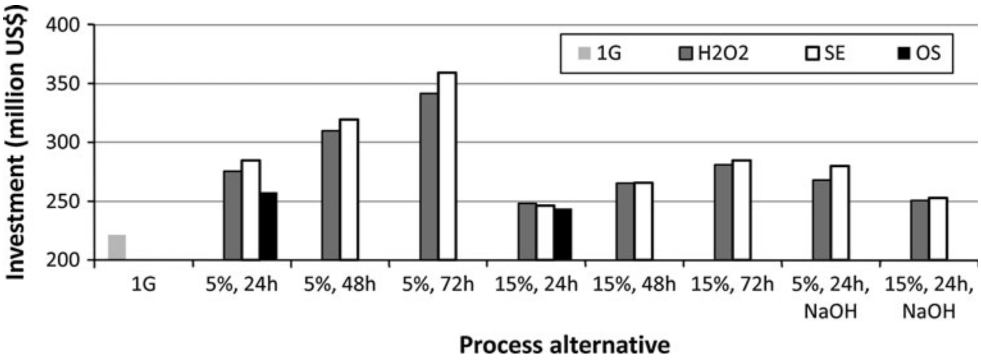


Fig. 6 Ethanol and surplus electricity production and average internal rate of return (*IRR*) for the integrated 1G and 2G bioethanol—selected scenarios

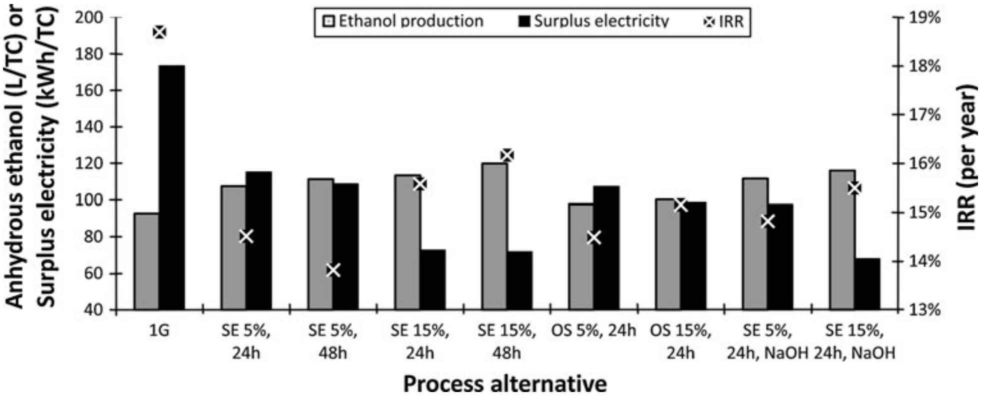
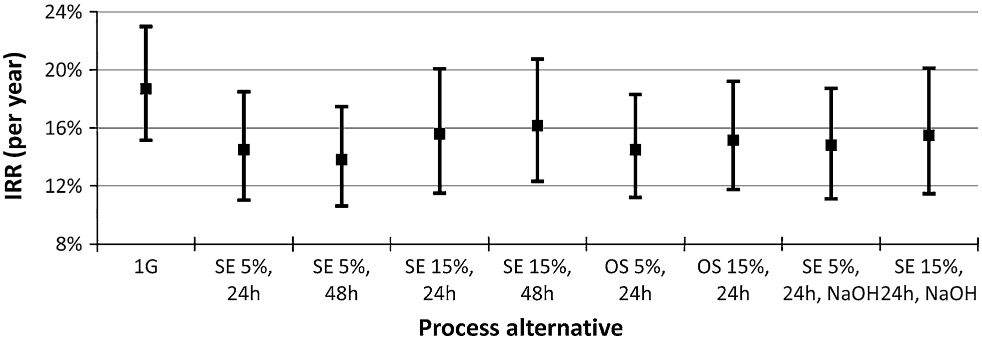


Fig. 7 Internal rate of return (*IRR*) of selected scenarios: 99.7% confidence interval



production. A normal distribution of overall investment, ethanol and electricity average prices, sugarcane, sugarcane trash, chemicals and enzyme average costs, presented in Table 6, was assumed for each alternative, considering 10,000 possible scenarios with random combinations of these variables.

It was verified that in order to achieve similar IRR values obtained for steam explosion or organosolv pretreatments, the hydrogen peroxide pretreatment requires that the catalyst (H_2O_2) price be reduced to 5% of its original value, or the ethanol price paid to the producer must be raised extremely (at least double that of the other alternatives). Thus, results for the economic evaluation of the integrated process with hydrogen peroxide pretreatment are not presented. In addition, due to the massive installed capacity of hydrolysis reactors required for the integrated processes with 72 h of hydrolysis, their results of the economic analyses are also omitted.

The results obtained for the average internal rate of return (IRR) on each scenario is illustrated in Fig. 6, and in Fig. 7 the IRR for a 99.7% confidence interval is presented.

Results in Figs. 6 and 7 for the steam explosion pretreatment with 5% solids load on hydrolysis (SE 5% 24/48 h) present a decrease of the IRR value, in spite of an increase in hydrolysis time. This is due to the fact that, for dilute solutions, an increase in hydrolysis time requires larger investments and provides few gains in overall ethanol production. Thus, increasing hydrolysis time (and

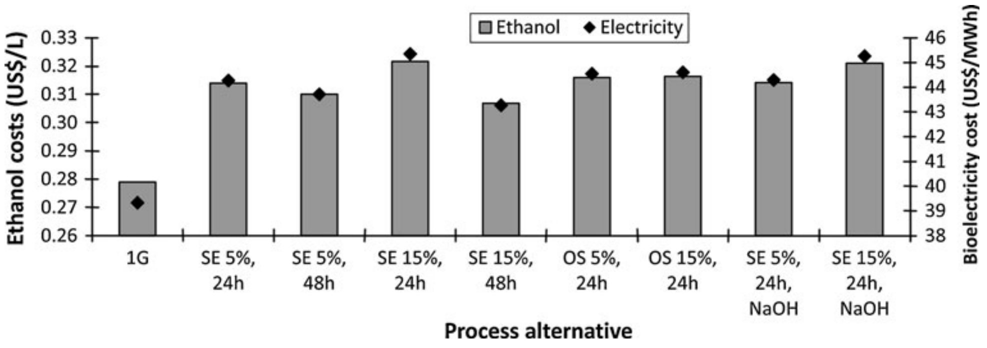


Fig. 8 Ethanol and surplus electricity costs for the bioethanol production process—selected scenarios

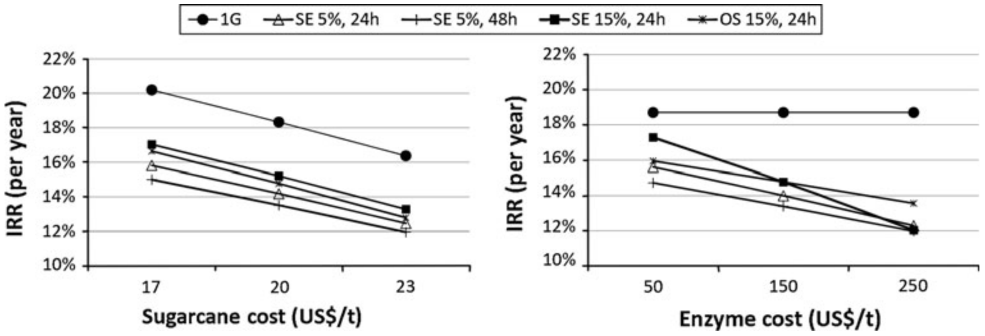


Fig. 9 Sensitivity analyses: impact of sugarcane and enzyme costs on the internal rate of return (*IRR*)

consequently, its yields) does not necessarily lead to an increase in process profitability; other factors, such as solids loading on hydrolysis, must be addressed.

Ethanol and surplus electricity production costs were evaluated, proportionally decreasing the prices of both products until the internal rate of return is equal to zero. Results for calculated production costs are shown in Fig. 8.

Several sensitivity analyses were performed as well. Sugarcane and enzyme costs have significant impact on the IRR of the integrated process. Results for these two sensitivity analyses are shown in Fig. 9.

It can be observed that large (66%) changes in the enzyme cost leads to similar impacts on the IRR as relatively small (15%) changes on sugarcane costs. Therefore, research towards development of sugarcane varieties that lead to decreased sugarcane costs may eventually yield greater economic gains than decreases in enzyme costs.

Conclusions

In this work, simulations of the integrated bioethanol production process from sugarcane, bagasse and trash were carried out using the SuperPro Designer process simulator. Selected pre-treatment methods (steam explosion, hydrogen peroxide and organosolv) followed, or not, by an alkaline delignification step were evaluated, along with the subsequent enzymatic hydrolysis step, considering different solids loading on hydrolysis (5 or 15%) and hydrolysis length (24, 48 or 72 h). The amount of lignocellulosic material available for hydrolysis was determined for each configuration, considering that the thermal requirements of the integrated plant are supplied by using part of the lignocellulosic material as fuel in boilers. An economic risk analysis was carried out, allowing evaluation of the internal rate of return of each scenario. Similar results for overall ethanol production for the integrated first and second generation processes with both hydrogen peroxide and steam explosion pretreatments were obtained for the same process conditions (solids loading and hydrolysis time). Performing hydrolysis for long periods (72 h) requires extremely large hydrolysis reactors and provides only small increments on yield; thus, the best conditions for 2G production integrated with the conventional 1G process seems to be those that consider around 24–48 h of hydrolysis and increased solids loading on the hydrolysis reactor. The amount of catalyst used in the hydrogen peroxide pretreatment and its price must be reduced in order for the process to become feasible. The 2G production process must be improved (e.g. decreasing investment, improving yields, developing pentose fermentation to ethanol) in order to improve competitiveness of 2G integrated with 1G production process, reaching higher forecasted IRR values.

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