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TASSIA LOPES JUNQUEIRA

"TECHNO-ECONOMIC FEASIBILITY ANALYSIS OF PROCESS ALTERNATIVES FOR ETHANOL PRODUCTION IN BRAZIL"

"ANÁLISE DE VIABILIDADE TÉCNICO-ECONÔMICA DE ALTERNATIVAS DE PROCESSO PARA A PRODUÇÃO DE ETANOL NO BRASIL"

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UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Engenharia Química

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Thesis presented to the School of Chemical Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Chemical Engineering.

Tese apresentada à Faculdade de Engenharia Química da Universidade Estadual de Campinas como parte dos requisitos exigidos para obtenção do título de Doutora em Engenharia Química.

Supervisor/Orientador: Prof. Dr. RUBENS MACIEL FILHO

Co-Supervisor/Coorientador: Dr. ANTONIO M. F. L. J. BONOMI

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Techno-economic feasibility analysis of process alternatives for ethanol production in Brazil

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ABSTRACT

Sugarcane mills fit into the biorefinery concept, since ethanol, sugar and electricity, among others, are possible products. The first generation (1G) ethanol production, from sugarcane juice, is a well-established process, while ethanol production from lignocellulosic materials, the so-called second generation (2G) process, has received special attention in the last decades. In Brazil, sugarcane bagasse and straw are potentially the most important feedstock for 2G ethanol production due to their availability and relative low cost, but the process is not established yet.

This study focused on the integration of different technologies in the ethanol production process, taking into account both 1G and 2G technologies, in order to assess the impacts on techno-economic feasibility of sugarcane biorefineries.

Results showed that product diversification, through production of sugar, electricity and biogas, as well as production flexibility improve techno-economic feasibility and reduce susceptibility to market oscillations, improving business stability.

For 2G ethanol production, the impacts of operating conditions on enzymatic hydrolysis and enzyme features in the integrated 1G2G ethanol production process were assessed through the formulation of a mathematical model and statistical evaluation. Aiming at the reduction of ethanol production cost, best operating conditions were determined and showed to be very sensitive to enzyme prices.

Extending the operation period of sugarcane biorefineries, which is from 6 to 8 months per year, allows reducing contribution of investment on ethanol production cost. Sweet sorghum, processed in the sugarcane off-season, presented a great potential to increase ethanol and electricity production as well as to improve economic feasibility. Integration of a 2G plant processing all year-round resulted in a promising alternative, but presents high investment cost compared to other alternatives.

The approach presented in this thesis can be used to perform assessments of other routes and technologies, identifying technological bottlenecks and guiding research in order to improve process feasibility.

Keywords: Biorefineries - Brazil, Ethanol, Process Simulation, Economic Feasibility.

RESUMO

As usinas de cana-de-açúcar encaixam-se no conceito de biorrefinaria, uma vez que produzem etanol, açúcar e eletricidade, entre outros produtos. A produção de etanol de 1ª geração (1G), a partir do caldo de cana-de-açúcar, é um processo bem estabelecido, enquanto a produção de etanol a partir de materiais lignocelulósicos, denominado processo de 2ª geração (2G), tem recebido atenção especial nas últimas décadas. No Brasil, bagaço e palha são as matérias-primas de maior potencial para a produção de etanol 2G devido a sua disponibilidade e relativo baixo custo, no entanto o processo não está consolidado até o momento.

O presente estudo teve por objetivo estudar a integração de diferentes tecnologias ao processo de produção de etanol, considerando as tecnologias 1G e 2G, a fim de avaliar os impactos na viabilidade técnico-econômica das biorrefinarias de cana-de-açúcar.

Resultados mostraram que a diversificação dos produtos, através da produção de açúcar, eletricidade e biogás, bem como a flexibilidade na produção melhoram a viabilidade técnico-econômica e diminuem a suscetibilidade às oscilações de mercado, aumentando a estabilidade dos negócios.

Para a produção de etanol 2G, os impactos das condições operacionais da hidrólise enzimática e características das enzimas no processo integrado de produção de etanol 1G2G foram avaliados através da formulação de um modelo matemático e análise estatística. Visando à redução do custo de produção do etanol, as melhores condições operacionais foram determinadas e mostraram-se muito sensíveis ao preço de enzimas.

A extensão do período de operação das biorrefinarias de cana-de-açúcar, que é usualmente de 6 a 8 meses por ano, permite reduzir a contribuição do investimento no custo de produção de etanol. O processamento de sorgo sacarino durante a entressafra de cana-de-açúcar apresentou expressivo potencial para incrementar a produção de etanol e eletricidade, bem como melhorar a viabilidade econômica. A integração de uma planta 2G processando o ano todo resultou em uma alternativa promissora, mas com alto investimento quando comparada às demais alternativas.

A abordagem apresentada nesta tese pode ser utilizada para avaliar outras rotas e tecnologias, identificando gargalos tecnológicos e guiando a pesquisa a fim de aumentar a viabilidade do processo.

Palavras-chave: Biorrefinarias - Brasil, Etanol, Simulação de Processos, Viabilidade Econômica.

CONTENTS

Dedico aos meus pais,
meus irmãos e meu marido.

To my parents, my siblings
and my husband.

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"To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advances in science"

Albert Einstein

Nomenclature

List of Acronyms and Abbreviations

1G – first generation

1G2G – first and second generation

2G – second generation

ABE – acetone-butanol-ethanol

ANEEL – Brazilian Electricity Regulatory Agency

BM – Boston-Mathias alpha function

BNDES – Brazilian Development Bank

C5 – pentoses

C6 – glucose

CAPEX – capital expenditure

CCD – central composite design

CEPCI – Chemical Engineering Plant Cost Index

CEPEA – Center for Advanced Studies on Applied Economics

CGEE – Center for Strategic Studies and Management

CHP – combined heat and power generation

COD – chemical oxygen demand

CONAB – National Supply Company

CTBE – Brazilian Bioethanol Science and Technology Laboratory

DOE – design of experiments

EL – enzyme loading

EP – enzyme price

EPE – Energy Research Company

FFV – flex fuel vehicles

FPU – filter paper unit

GHG – greenhouse gas

HMF – hydroxymethylfurfural

HOC – Hayden-O'Connell

HT – hydrolysis time

HTM – high test molasses

IEA – International Energy Agency

IPCA – Extended National Consumer Price Index

IRR – internal rate of return

LCA – life cycle assessment

LCM – lignocellulosic material

LHV – lower heating value

MAPA – Brazilian Ministry of Agriculture, Livestock and Supply

MARR – minimum acceptable rate of return

MCTI – Ministry of Science, Technology and Innovation

MEPC – minimum ethanol production cost

MME – Ministry of Mines and Energy

NPV – net present value

NREL – National Renewable Energy Laboratory (United States)

NRTL – Non-Random Two-Liquid

OPEX –operational expenditure

RK – Redlich-Kwong

RKS – Redlich-Kwong-Soave

SC – solids content

SSF – simultaneous saccharification and fermentation

TC – tonne of cane

TRS – total recoverable sugars

tSHF – time separated hydrolysis and fermentation

U.S. – United States

UASB – up-flow anaerobic sludge blanket

VHP – very high polarization (sugar specification)

VSB – Virtual Sugarcane Biorefinery

List of Symbols

f_{CH4}– volumetric fraction of methane in biogas

η_{biod} – removal efficiency of chemical oxygen demand

Ω_{CH4} – volume of methane produced per mass of removed chemical oxygen demand

Q_{biogas}– biogas volumetric flow

$Q_{vinasse}$– vinasse volumetric flow

1. Introduction

Nowadays, one of the greatest concerns in the world regards the large scale production of alternative forms of energy, such as biofuels, which could reduce greenhouse gases emissions and improve energy security when compared to their fossil counterparts (CHAVEZ-RODRIGUEZ; NEBRA, 2010). Biofuels include bioethanol, biomethanol, biodiesel, biogas, biosynthetic gas (bio-syngas), bio-oil, biochar, Fischer-Tropsch liquid biofuels, and biohydrogen (BALAT, 2011). Among them, bioethanol has received special attention, as it is already produced and used as automotive fuel in large scale (SEABRA et al., 2010).

In Brazil, conventional ethanol production is based on sugarcane juice fermentation, which is known as first generation (1G) production process. This process takes place in annexed plants and autonomous distilleries; the latter produces ethanol and electricity and the former produces sugar in addition to these products. In 2011/2012 season, approximately 64 % of the sugarcane processing units in Brazil were annexed plants (CONAB, 2013). The capability of plants to produce both ethanol and sugar had a great influence on the success of ethanol production in Brazil, since synergies and complementary relationships between the sugar and ethanol production processes reduce costs and increase the efficiency of agro-industrial processes (BNDES; CGEE, 2008). For instance, coupling the sugar and ethanol production processes allows the use of molasses, a concentrated residual solution generated during sugar crystallization. Molasses may be added to sugarcane juice, raising sugar concentration close to the levels required by the fermentation process.

While sugarcane juice is destined to sugar and ethanol production, sugarcane bagasse is generally used as fuel in the boilers, providing heat and power to the industrial plant. When generated electricity exceeds the process demand, and the plant is located close to an electricity grid, it can be exported.

Another possibility for the use of sugarcane bagasse is as feedstock in the production of second generation (2G) ethanol, also known as cellulosic ethanol. The utilization of lignocellulosic materials for ethanol production stands out as a promising alternative for large scale production of biofuels for transportation sector. In this context, agricultural residues (such as corn stover, sugarcane residues, wheat or rice straw), forestry and paper mill discards, solid municipal wastes and dedicated energy crops (e.g. energy cane and biomass sorghum) can be converted to ethanol (LIN; TANAKA, 2006).

Bearing in mind the projected expansion in the production and consumption of ethanol, the use of bagasse as feedstock is especially attractive since it does not compete with food crops and is less expensive than conventional agricultural feedstocks (ALVIRA et al., 2010). If integrated to 1G plants, 2G ethanol production process can share part of the 1G infrastructure, such as juice concentration, fermentation, distillation, cogeneration and water cooling systems. Another important residue that may be employed for ethanol production is the sugarcane straw, which includes sugarcane leaves and tops, usually burnt or left in the field (DIAS et al., 2011; MACRELLI et al., 2012). With the restriction to burn the sugarcane straw, such material can be recovered from the field to be used as feedstock. The amount of straw that must be left on the field depends on specific conditions of the sugarcane field, such as location, cane variety, stage of cut, harvesting period, climate and other combined aspects (HASSUANI et al., 2005).

The use of sugarcane bagasse and straw as feedstock for 2G ethanol production motivates the energy optimization of 1G plant, since reduction of steam consumption leads to a decrease of the bagasse and straw burnt to produce energy, increasing lignocellulosic material availability for 2G process and overall ethanol production (DIAS et al., 2012a).

Besides the great potential as fuel, ethanol can also be used as raw material for production of chemicals, which consists in the alcoholchemistry route. In fact, most of the chemicals derived from petroleum can be obtained from ethanol, especially ethylene used for resins production as well as other ethanol-derived products, such as acetates and ethyl ether, that are usually imported (BASTOS, 2007).

1.1. Objectives

The purpose of this thesis was to assess alternative configurations of sugarcane biorefineries focusing on the increase of techno-economic feasibility of ethanol production in Brazil. This assessment was performed through process simulation, including sugarcane biomass processing to ethanol and other products as well as energy generation. Economic engineering impacts were calculated and used to compare the alternative process configurations.

The research was divided as follows:

- Assessment of sugar, electricity and biogas co-production in a first generation biorefinery;
- Evaluation of operational conditions and enzyme features in the integrated first and second generation ethanol production;
- Comparison of process configurations and feedstock alternatives for extension of operational period in sugarcane biorefineries.

1.2. Outline of this thesis

In Chapter 2, the history and current scenario for ethanol market and the sugar-energy industry as well as relevant data and statistics are reviewed. Descriptions of 1G and 2G ethanol production processes, biodigestion process and alternatives for extending sugarcane biorefineries operating period are presented, showing some practical examples in the sugar-energy industry. In addition, a review of studies using process simulation and economic evaluation related to ethanol production process and other biorefinery alternatives is presented in this chapter.

In Chapter 3, a comprehensive description of methodology and assumptions used as basis for the development of this work is presented, including representation of unit operations in the process simulation software (Aspen Plus®), estimation of investment data and definition of economic indicators.

Chapters 4, 5 and 6 organize results and discussion through the following manuscripts, respectively.

- **Sugarcane biorefinery: product diversification impacts on first generation ethanol feasibility** *(draft version)*.
- **Junqueira, T. L.**; Morais, E. R.; Rivera, E. C.; Carli, C. M.; Maciel Filho, R.; Pradella, J. G. C.; Bonomi, A. **Which enzyme are we looking for? A screening design approach**

to analyze enzyme influence on the feasibility of second generation ethanol. Submitted to Biocatalysis and Biotransformation *(under review).*

- **Process configurations and feedstock alternatives to extend the operational period of sugarcane biorefineries** *(draft version).*

Chapter 4 focuses on the validation of the methodology by assessing technologies already available in the sugar-energy industry, such as sugar production and high pressure boilers to increase electricity generation, and vinasse biodigestion, although it is not as disseminated as the other technologies.

In Chapter 5, the evaluation of 2G ethanol production, through development of a mathematical model and statistical analysis, presents another possible approach that consists of identifying process bottlenecks to guide research and development.

Chapter 6 presents techno-economic assessment of alternatives for extending operation in sugarcane biorefineries in order to provide information to the sector towards year-round operation and increased profitability.

Conclusions and suggestions for future work are presented in Chapter 7.

1.3. List of related publications

In this thesis, some results presented in the following publications are organized and updated in order to provide a comparison of the alternatives assessed during the development of this study. The author of this thesis contributed in these publications mainly on the discussion of scenarios (definition and interpretation), consultation of available scientific literature, development of process simulations and discussion of the obtained impacts.

- **Junqueira, T. L.**; Dias, M. O. S.; Jesus, C. D. F.; Mantelatto, P. E.; Cunha, M. P.; Cavalett, O.; Maciel Filho, R.; Rossell, C. E. V.; Bonomi, A. **Simulation and Evaluation of Autonomous and Annexed Sugarcane Distilleries**. Chemical Engineering Transactions, 25, 941-946, 2011.

- 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. **Environmental and economic assessment of sugarcane first generation biorefineries in Brazil**. Clean Technologies and Environmental Policy, 14 (3), 399-410, 2012.
- Cavalett, O., Cunha, M. P., Chagas, M. F., **Junqueira, T. L.**, Dias, M. O. S., Pavanello, L. G, Leal, M. R. L. V., Rossell, C. E. V, Bonomi, A. **An exploratory economic analysis of sugarcane harvest extension using sweet sorghum in the Brazilian sugarcane industry**. XXVIII ISSCT Congress, São Paulo, Brazil, 2013.
- Moraes, B. S, **Junqueira, T. L.**, Pavanello, P. G., Cavalett, O., Mantelatto, P. E., Bonomi, A., Zaiat, M. **Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense?** Applied Energy, 113, 825–835, 2014.

1.4. Contribution of the thesis

This work provided an overview of technological alternatives that already exist (to a greater or lesser extent) in sugarcane mills or are in development stage. Techno-economic assessment was carried out considering greenfield projects, i.e. new facilities; thus overall investment was taken into account instead of incremental investment.

The assessment, using the same methodology, process parameters, economic assumptions and prices, enabled to establish a basis for comparison that offers ground for decision making process. In addition, integration of these alternatives in the first generation ethanol process was particularly useful, since the analysis of a specific process step may lead to conclusions that are different from those obtained in the assessment of the entire process.

2. Literature Review

2.1. Ethanol market and sugar-energy industry

United States (U.S) and Brazil are the main players in the ethanol market, being responsible for 80 % of the world production and commercialization. U.S. is the largest ethanol producer worldwide, having produced 50 billion liters of ethanol in 2013, while Brazilian production was approximately 28 billion liters (EPE, 2014). Figure 1 presents ethanol production in Brazil for the last decades.

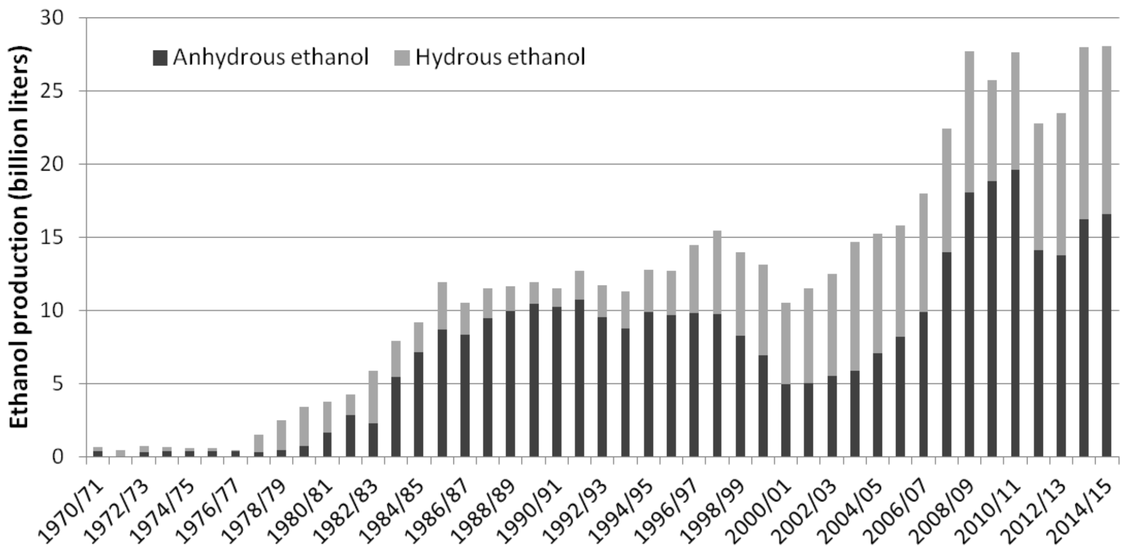

Figure 1. Anhydrous and hydrous ethanol production in Brazil (data from MAPA, 2013; 2015).

In Brazil, ethanol production was first encouraged by a national program, the PROALCOOL, created in 1975. At that time, the country was strongly dependent on imported oil and gasoline was the main oil derivative consumed. As a result of the program implementation, new distilleries were annexed to the existing sugar mills in the first five years and, in the 1979-1985 period, many autonomous distilleries were built. An accentuated increase on ethanol production was observed in this period (see Figure 1). However, in the 1990s the liberalization of fuel prices to consumers and full deregulation of sugarcane industry led to the end of PROALCOOL with discontinuation of government support (WALTER; DOLZAN, 2012).

Ethanol sector experienced another growth with the introduction of flex-fuel vehicles (FFVs) in the automotive market in 2003. The FFVs are capable of operating on hydrous ethanol, gasoline or any proportion between these fuels (SCANDIFFIO, 2005). As a consequence, after the 2005/06 season, the production of hydrous ethanol exceeded anhydrous ethanol, which is blended to gasoline. Recently, Brazilian government has decided to increase the mix of ethanol in gasoline from 25 to 27 % starting in 2015; as a result, an increase on annual anhydrous ethanol consumption of one billion liters is estimated (FERNANDES, 2015).

Historically, sugar and ethanol present a high interdependence, since most Brazilian sugarcane facilities produce both products. These facilities, called annexed plants, usually have a small flexibility (around 15 %) to produce more sugar or ethanol aiming at the increase of profitability. This synergy, at the same time that allows reducing production costs and risks, makes ethanol production more susceptible to changes, reducing its participation on the production mix when sugar market is more attractive (EPE, 2014). Nowadays, about 70 % of Brazilian sugar production is destined to exportation, which corresponds to about half of world sugar export (CONAB, 2013).

Destination of sugars to each product, for the last decades, is shown in Figure 2.

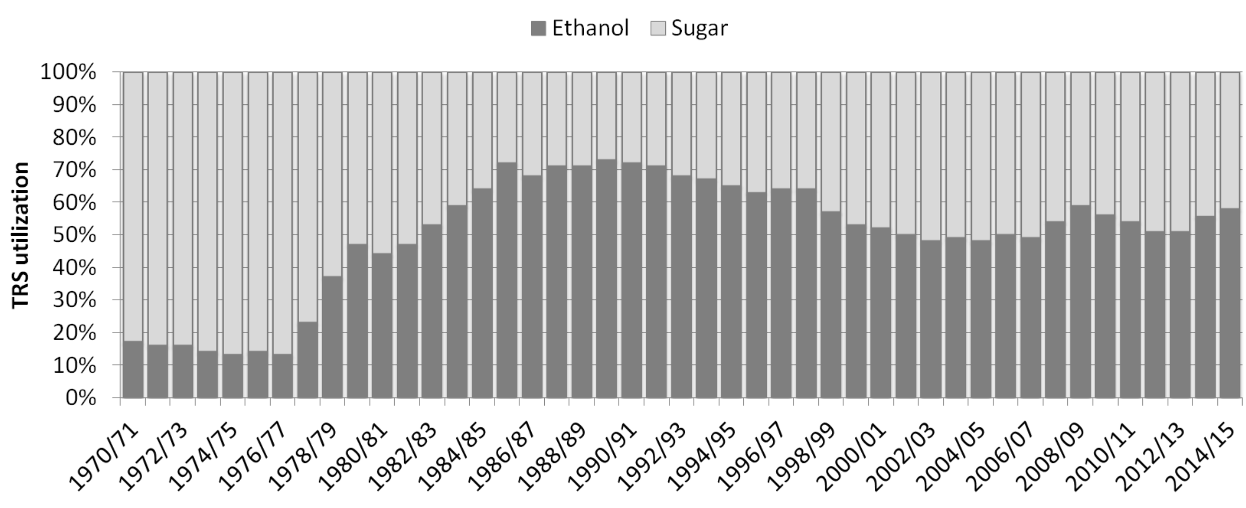

Figure 2. Total recoverable sugars (TRS) utilization for ethanol and sugar production in Brazil (data from MAPA, 2013; 2015).

From the end of 1970s to late 1980s, during the PROALCOOL period, destination of sugars to ethanol production significantly increased (above 70 %). In the following decade, small changes in the production mix were observed favoring sugar production. In the 2000s, a more accentuated increase on sugar production led to equilibrium between ethanol and sugar production mix.

Between 2008 and 2014, 83 Brazilian sugarcane mills ceased their operation due to financial difficulties (VEJA, 2015). The shutdown of industrial plants, in addition to a restructuration process with mergers and acquisitions and lack of investments in new industrial plants – as a consequence of 2008 global crisis – led to a decrease on the number of sugarcane facilities. Besides, reduction of investments in renewal of sugarcane plantations, unfavorable climate conditions and increase on sugar losses due to mechanization also contributed to decrease sugarcane productivity and ethanol competitiveness (EPE, 2014).

However, a partial recovery of sugarcane productivity in 2011/2012 season – motivated by the increase on agricultural investments – and reduction of international sugar prices alleviated this scenario, decreasing ethanol production costs and recovering its competitiveness (EPE, 2014).

In addition, electricity was consolidated as a third product in sugarcane facilities, reducing the risks associated to the sugar-energy sector. The electricity from sugarcane biomass was introduced in the national energy matrix through public commercialization auctions. The possibility to sell energy to the grid, in addition to elevated electricity prices, has motivated investments on more efficient cogeneration systems and complementary biomass use (such as sugarcane straw and energy cane) in order to increase electricity generation and competitiveness. Currently, electricity from sugarcane biomass and ethanol represent almost 18 % of primary energy production and 38 % of renewable energy produced in Brazil (EPE, 2013).

2.2. First generation (1G) ethanol production

First generation process is based on the conversion of extractable sugars and starch into ethanol. In the sugar-to-ethanol process, sucrose is obtained from sugar crops such as sugarcane, sugar beet and sweet sorghum, and is subsequently fermented to ethanol. Ethanol production from starch-based feedstock – e.g. corn, wheat and cassava – is more complex and costly, since it requires additional steps for hydrolysis of starch into glucose before fermentation to ethanol, besides the need of an external source to produce the energy required in the process. Ethanol is mostly produced from corn and sugarcane in the U.S. and Brazil, respectively. Smaller amounts are produced in Europe using wheat and sugar beet as feedstock (FERREIRA-LEITÃO et al., 2010; IEA, 2011).

Brazilian sugarcane industry is energy self-sufficient, producing all steam and electricity required in the process and, in some cases, even selling electricity surplus to the grid. For each unit of fossil energy used in its production, sugarcane ethanol generates approximately 9 units of renewable energy (and potentially 11.6 if optimization features are considered); for U.S. corn ethanol, this relation is between 1.9 and 2.3 (MACEDO et al., 2008; MILANEZ et al., 2014).

In addition, Brazilian sugarcane facilities fit into the biorefinery concept, since ethanol, sugar and electricity can be produced from sugarcane. A biorefinery integrates biomass conversion processes and equipment to produce biofuels for mobility, power, and chemicals from biomass. This concept is analogous to a petroleum refinery, which produces multiple fuels and products from petroleum (CHERUBINI, 2010).

In Brazil, ethanol production process takes place in annexed plants and autonomous distilleries; the latter produces ethanol and electricity and the former also produces sugar (CAVALETT et al., 2012). Conventional ethanol production process consists of sugarcane reception, cleaning and preparation, sugar extraction, juice treatment and concentration, fermentation, distillation and ethanol dehydration. Additionally, sugar crystallization and drying are required in the annexed plants. In both plants, a cogeneration system, also known as combined heat and power generation unit (CHP), produces steam and electricity to supply the process and, in some industrial units, the electricity surplus is sold to the grid. Figure 3 shows a block flow diagram representing an autonomous distillery and an annexed plant.

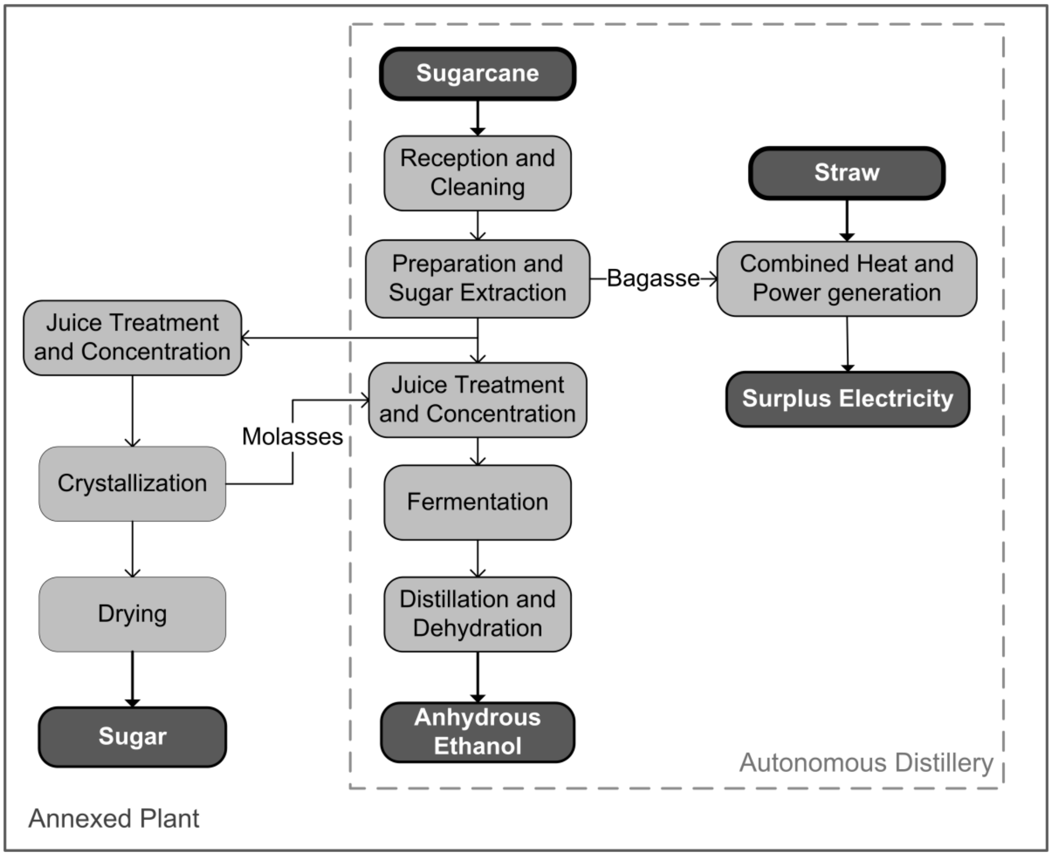

Figure 3. Schematic block flow diagram for autonomous distillery (dashed box) and annexed plant (external box).

A brief description of the process steps involved in the sugarcane industrial plants is presented below. More information and process parameters can be seen in Chapter 3.

Sugarcane reception and cleaning

The sugarcane delivered to the mill contains mineral and vegetable impurities in quantities that vary depending on the harvesting system (manual or mechanical), type of soil and climate conditions, among other factors (ALBARELLI, 2013). In order to remove these impurities, sugarcane is washed (for whole stalks) or submitted to a dry cleaning step (for chopped cane). In view of the harvest mechanization, dry cleaning is being introduced in the sugarcane mills to reduce sugar losses (CGEE, 2009).

Sugarcane preparation and sugar extraction

After cleaning, sugarcane is fed to a preparation system, on which a series of equipment (knives, shredders, hammers, etc.) are used to cut open the sugarcane structure and enhance sugar extraction (CGEE, 2009).

Sugar extraction is traditionally carried out using mills, but diffusers are being gradually introduced in the plants. In both processes, water is added to improve extraction of sugars that are recovered in the juice. In mills, extraction is performed using successive and gradual compression stages; while diffusers are based on diffusion and lixiviation and require final dewatering stages (OLIVERIO et al., 2013). In both cases, bagasse, the fibrous residue with moisture content around 50 %, is sent to the cogeneration system to be used as fuel in the boilers.

Juice treatment and concentration

In order to remove impurities, the extracted juice undergoes a series of operations: screening, heating, liming, flocculation, settling and filtering. Additional operations and inputs may be required depending upon the product specifications (MANTELATTO, 2005). Then, the resultant liquid stream, known as clarified juice, is concentrated in evaporators. In autonomous distilleries, a single step evaporator concentrates the juice around 22 °Brix (% of soluble solids); while in annexed plants, concentration is carried out in multiple-effect evaporators to produce syrup (65 °Brix). An important treatment by-product is the filter cake that is used as fertilizer in the field.

Sugar crystallization and drying

In annexed plants, the syrup is further evaporated in vacuum pans until saturation, followed by crystallizers where sugars are recovered as crystals. Sugar crystals are dried and cooled to be stored. The liquid fraction after crystallization, containing mainly sucrose and reducing sugars, is called molasses and is used for ethanol production (CTBE, 2012).

Fermentation

In the ethanol production process, juice (and molasses, in annexed plants) is sent to the fermentation process, where sugars (sucrose and reducing sugars) are converted to ethanol using yeast (*Saccharomyces cerevisiae*). Although continuous fermentation is used in some industrial plants, fed-batch fermentation is still the most common process configuration. Yeast cells are centrifuged, treated with acid and recycled back to fermentation reactors, while the liquid fraction is sent to the distillation unit. Alternative technologies for fermentation process have been proposed, such as vacuum extractive fermentation and low temperature fermentation that allow the use of more concentrated feed (DIAS, 2011; ATALA, 2004).

Distillation and ethanol dehydration

The fermentation product, known as wine, contains an alcoholic content between 8 and 12 °GL (% in volume) and is sent to a series of distillation columns to obtain hydrous ethanol (around 93 wt%). Vinasse and phlegmasse, mostly composed by water, are obtained in the bottom of the columns and together represent the most voluminous effluents in the process. More volatile compounds are recovered as 2^{nd} grade alcohol, while higher alcohols and esters are concentrated as fusel oil.

Because water and ethanol form an azeotrope with 95.6 wt% ethanol at atmospheric pressure, conventional distillation cannot achieve the separation required to produce anhydrous ethanol, and alternative separation processes are necessary. The most common dehydration methods in the sugarcane mills are: azeotropic distillation with cyclohexane, extractive distillation with monoethyleneglycol (MEG) and adsorption onto molecular sieves (JUNQUEIRA, 2010). In addition, pervaporation technology (membranes) is already commercial and presents great potential to reduce steam consumption in ethanol dehydration process (SERMATEC, 2015).

Cogeneration system (combined heat and power generation)

In the cogeneration system, bagasse is usually burnt in the boilers, which generate steam to drive back-pressure turbines coupled to an electric generator. Low-efficiency boilers, generating steam at around 22 bar pressure, and high steam consumption in the process are strong limiting factors to surplus electricity generation. Recently, higher temperature and pressure levels of steam generated in the boilers and use of extraction-condensing turbines allowed increasing the surplus electricity generated, which can be sold to the grid (ENSINAS et al., 2014).

2.3. Second generation (2G) ethanol production

The utilization of lignocellulosic materials for ethanol production – known as second generation ethanol or cellulosic ethanol production – stands out as a promising alternative for biofuels production in large scale. In this context, agricultural residues (such as corn stover, sugarcane residues, wheat or rice straw), forestry and paper mill discards, municipal solid waste and dedicated energy crops (e.g. energy cane and biomass sorghum) can be converted to ethanol (LIN; TANAKA, 2006).

Although these materials present advantages such as lower cost and less competition with food, the technologies required for their conversion to ethanol are more complex and costly than those of the first generation process, using sugarcane, corn and sugar beet as feedstock (MARTÍN; THOMSEN, 2007; MUSSATTO et al., 2010; ALVIRA et al., 2010). This complexity is due to the fact that lignocellulosic materials – composed of carbohydrate polymers (cellulose and hemicellulose), lignin and, in a lesser extent, extractives and minerals – do not contain monosaccharides readily available for bioconversion (through fermentation); thus they have to be hydrolyzed, by means of acids or enzymes, to fermentable sugars (MARTÍN et al., 2007).

In Brazil, 2G ethanol production is focused on the use of sugarcane lignocellulosic fractions: bagasse and straw (tops and leaves). These residues account for approximately two thirds of the energy content of the whole sugarcane biomass, and their use as feedstock allows increasing ethanol production using the same crop area.

Bagasse is already available at sugarcane processing facilities, but higher amounts may be accessible if improved cogeneration technologies and more energy efficient processes are employed, since part of bagasse is used as fuel to provide energy to the process. In addition, increasing quantities of straw have been made available due to the transition of manual to mechanized harvest as consequence of the banishment of burning practices since the 2000s (HASSUANI et al., 2005).

Besides the lignocellulosic availability at the plant site, operation of 2G technology integrated to sugar/ethanol production units allows sharing part of the infrastructure, such as fermentation, distillation and cogeneration areas, as shown in Figure 4.

In Brazil, GranBio initiated the production of 2G ethanol in September/2014, which is the first commercial scale plant in the Southern Hemisphere. The plant, located in Alagoas/Brazil, has a production capacity of 82 million liters of ethanol per year (GRANBIO, 2014). Two months later, Raízen completed the construction of a 2G plant in São Paulo/Brazil that will have capacity to produce 40 million liters per year (RAÍZEN, 2015).

The basic steps of the biochemical conversion of biomass to ethanol include pretreatment, enzymatic hydrolysis and fermentation. Alternatively, C5 liquor biodigestion may be considered for pentoses destination producing biogas to be used as complementary fuel. A brief description is presented below, including the main concepts and challenges for each 2G process step.

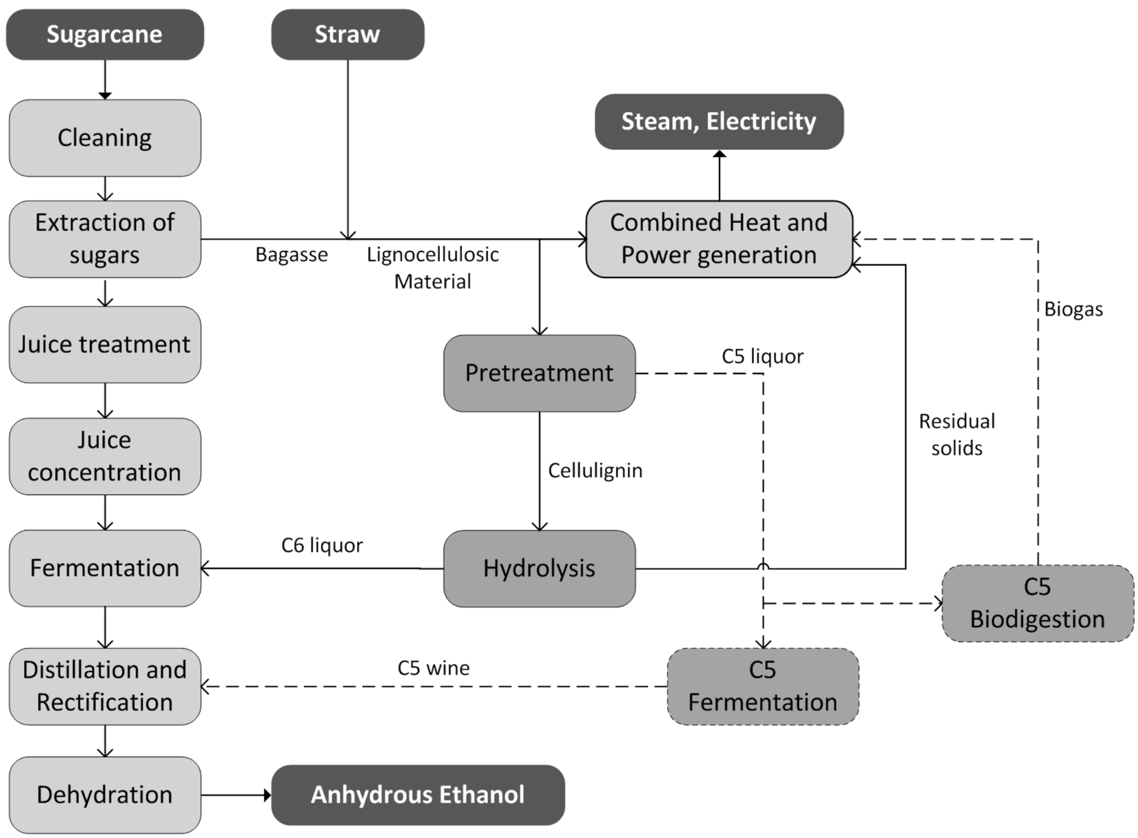

Figure 4. Integration of 2G process in a 1G autonomous distillery.

<u>Pretreatment</u>

Cellulose in plants is closely associated with hemicelluloses and lignin, preventing the access of hydrolytic agents to cellulose. Unless a very large excess of enzyme is used, the enzymatic digestibility of cellulose in native biomass is low (< 20 % yield). For this reason, pretreatment process is required to alter the structure of the biomass, increasing cellulose accessibility to the enzymes that convert the carbohydrate polymers into fermentable sugars (MOSIER et al., 2005; MARTÍN et al., 2007).

Several alternatives for pretreatment have been proposed in the last decades, including biological, physical, chemical and physico-chemical processes as well as combination of these methods (ALVIRA et al., 2010). Several reviews on pretreatment methods are available in the literature (MOSIER et al., 2005; KUMAR et al., 2009; SILVA et al., 2013).

An efficient pretreatment method increases the formation of sugars in the subsequent enzymatic hydrolysis and avoids carbohydrates degradation and inhibitors formation. In addition, low equipment cost and energy requirements are other desirable features (SUN; CHENG, 2002; YANG; WYMAN, 2008).

It is important to highlight that the selection of the pretreatment depends on the feedstock used. In other words, a technology that is efficient for a particular type of biomass might not work for another material or require different operating conditions to achieve the same results (KUMAR et al., 2009).

In order to define the pretreatment method and conditions (e.g., acid concentration, temperature, pressure, severity factor), the chosen configuration for the subsequent steps must be taken into account, since it has large impact in cellulose digestibility (enzymatic hydrolysis), generation of toxic compounds potentially inhibitory for yeast (fermentation), energy demand in the downstream process (distillation) and, consequently, affects overall process yield (ALVIRA et al., 2010; GALBE; ZACCHI, 2007; MOSIER et al., 2005). For instance, the destination of hemicellulose has a great influence, since optimal pretreatment conditions for hemicellulose recovery are usually not the same as those for ethanol production from cellulose. During pretreatment, hemicellulose sugars may be degraded to weak acids and furan derivatives (GÍRIO et al., 2010), which can affect fermentation yield.

Considering a biorefinery concept, hexoses (C6 sugars, mostly glucose) could be fermented into ethanol, while pentoses (C5 sugars, mostly xylose) could be used for the production of a wide range of chemicals with higher added value. For this purpose, acid pretreatment, which releases mostly pentoses, as well as steam-based and liquid hot water processes that separate an oligosaccharides-rich stream are the most appropriated ones (SILVA et al., 2013). These pretreatments would also be applicable for separate C5 fermentation to ethanol; in this case, the C6 fraction, obtained after enzymatic hydrolysis, could be fermented with sugarcane juice using conventional yeast.

Steam explosion is one of the most common methods for the pretreatment of lignocellulosic biomass and can be performed in the presence or absence of a catalyst (alkali or acid). The biomass is treated with high-pressure saturated steam at temperatures varying from 160 to 260 °C in a pressurized system for a few seconds to 20 minutes, and then the pressure is quickly reduced, which makes the material undergo an explosive decompression (KARP et al., 2013; SILVA et al., 2013).

Enzymatic hydrolysis

The hydrolysis (or saccharification) of cellulose can be carried out through acid and enzymatic hydrolysis. Enzymatic hydrolysis has demonstrated better results for the subsequent fermentation because no degradation components of glucose are formed, since cellulase enzymes are highly specific (CARDONA et al., 2010; SUN; CHENG, 2002). The process is usually conducted at mild conditions (atmospheric pressure and temperature around 50 °C) and presents a relative long reaction time (from several hours to a few days). Characteristics of pretreated material, dosage and efficiency of the enzymes, residence time and solids content are some factors that influence the conversion in enzymatic hydrolysis (RABELO, 2010; ALVIRA et al., 2010).

The enzyme cost is usually mentioned as a concern in several works (MUSSATTO et al., 2010; SUN; CHENG, 2002; PANDEY et al., 2000; KLEIN-MARCUSCHAMER et al., 2012); therefore, cellulase recycling, other process configurations (e.g. simultaneous saccharification and fermentation) and on-site production of enzymes are proposed in order to reduce enzymatic hydrolysis costs.

For enzyme production, a large number of microorganisms including bacteria, yeasts and fungi have been studied, but filamentous fungi are the preferred choice (PANDEY et al., 2000). In the on-site enzyme production, the whole fermentation broth – containing fungal cells and substrate residues – is added to hydrolysis, avoiding expensive cell removal, enzyme concentration and purification steps (BARTA et al., 2010).

Fermentation

After enzymatic hydrolysis, hexoses and pentoses are released in the hydrolysate. Hexoses are readily fermented to ethanol by many naturally occurring organisms, but the pentoses are fermented to ethanol by few native strains, and usually at relatively low yields (MOSIER et al., 2005).

Saccharomyces cerevisiae is the microorganism traditionally used in ethanol production from sugarcane, presenting high efficiency in fermenting hexoses to ethanol, superior tolerance to ethanol and capacity to grow rapidly under the anaerobic conditions that are characteristically established in large-scale fermentation vessels (ZHANG et al., 2010; MUSSATO et al., 2010).

However, native strain of *S. cerevisiae* is not able to utilize pentoses, which is considered a drawback in 2G ethanol production, since the utilization of hemicellulosic fraction is pointed out as a determinant factor for the economic success of this novel route, reducing production costs and increasing ethanol production (GÍRIO et al., 2010; ALVIRA et al., 2010; SUN; CHENG, 2010).

Some yeasts present natural ability to ferment pentoses, such as *Scheffersomyces stipitis* (formerly known as *Pichia stiptis*), *Candida shehatae* and *Candida parapsilosis* (BALAT, 2011). *S. stipitis* has potential to ferment pentoses – obtained after pretreatment of biomass – into ethanol with high fermentation yields (AGBOBO et al., 2006).

Alternatively, metabolic engineering has been used to combine advantageous traits from different microorganisms in order to develop microorganisms able to efficiently convert sugars released by hydrolysis from lignocellulosic materials (ZALDIVAR et al., 2001). *Zymomonas mobilis*, *Saccharomyces cerevisiae* and *Escherichia coli* have been identified as the main microbial platforms in metabolic engineering/molecular biology for cellulosic ethanol production

(KUMAR et al., 2009). For instance, pentose fermenting strains of *S. cerevisiae* have been constructed using several metabolic engineering strategies involving the introduction of genes encoding for xylose and arabinose pathways from bacteria and fungi (MUSSATO et al., 2010).

The co-fermentation process represents another technological option for utilizing all the sugars released during biomass pretreatment and hydrolysis and consists in the use of a mixture of two or more compatible microorganisms that assimilate both hexoses and pentoses (CARDONA et al., 2010). In this context, Fu et al. (2009) proposed a fermentation scheme co-culturing immobilized *Z. mobilis* and free cells of *S. stipitis* for glucose and xylose fermentation, respectively. After the completion of glucose fermentation, the immobilized *Z. mobilis* is removed from the medium to avoid inhibition of xylose fermentation.

The presence of inhibitors represents an additional difficulty in the pentoses utilization, since hemicellulose may be degraded to weak acids and furan derivatives which potentially act as microbial inhibitors during the fermentation step to ethanol (GÍRIO et al., 2010). Formation of these substances is enhanced by acid addition and/or high temperatures. Some detoxification methods like neutralization, overliming with calcium hydroxide, activated charcoal, ion exchange resins and enzymatic detoxification using laccase are known for removing inhibitory compounds from lignocellulosic hydrolysates (CARDONA et al., 2010).

<u>1G2G Integration</u>

Integration between 1G and 2G processes can be accomplished in different levels, sharing only CHP unit for utilities generation or even part of the process. For instance, the product obtained after hydrolysis (rich in glucose) may be fermented mixed with sugarcane juice, thus decreasing the effects of potential inhibitors generated in second generation process (RIVERA et al., 2010). In the case C5 liquor is also fermented to ethanol, the resultant alcoholic streams may be mixed and sent to distillation and dehydration. However, there are still concerns on the disposal of vinasse from 2G process in the field, as currently done with 1G vinasse, due to the lower nutrients content and higher proportion of organic matter (MORAES et al., 2015).

In order to achieve the energy balance of the integrated plant, part of the lignocellulosic material is diverted to CHP along with the residual solids from hydrolysis. In this case, steam is produced only to meet process requirement and back-pressure turbines are employed.

2.4. Extending operation in sugarcane biorefineries

Sugarcane biorefineries operate from 6 to 8 months per year (from late March or April through late October or November in Center-South region) according to sugarcane harvesting period. Extended operation is desirable as it allows a better use of existing industrial capacity, reducing contribution of investment on production costs.

The first step to reduce idle capacity in sugarcane biorefineries is to operate the cogeneration system throughout the off-season period. Unlike systems with back-pressure turbines that need the process to condense the generated steam, the use of extraction-condensing turbines makes it possible to generate electricity during the off-season (ENSINAS et al., 2014). Alves (2011) found that electricity surplus obtained using all available bagasse in systems with extraction-condensing turbine is more than 2.5 times higher than those with back-pressure turbines that consumes bagasse only to meet process steam demand. In addition, for straw recovery rates of 50 %, it was possible to double the electricity generation compared to the same conditions when using only sugarcane bagasse. Other lignocellulosic materials, such as wood chips and energy grass, can also be used as complementary fuel in the boilers increasing electricity generation.

Santos (2012) evaluated different configurations for turbine systems and operation periods. The author concluded that the best alternative is the use of an extraction-condensing turbine, operating all year-round with minimum condensation in the season. This alternative presents reduced investment on cogeneration system, maintaining the annual electricity generation.

Techno-economic feasibility of the use of sugarcane biomass (surplus bagasse and straw) to produce surplus electricity all year-round showed great potential to increase electricity generation. However, straw recovery and processing costs as well as electricity prices are crucial factors for economic feasibility, making the business highly attractive or even not viable depending on the values considered (DEFILIPPI FILHO, 2013).

A practical example is the *Usina da Pedra*, a sugarcane mill in São Paulo State, that is recovering straw from the field (around 13 thousand tonnes in 2012), which allowed to increase the amount of bagasse stored for operation in the off-season period (FATOR BRASIL, 2013).

Based on the same idea of storing bagasse to operate cogeneration in the off-season, it is possible to concentrate and store sugarcane juice (known as high test molasses) to produce ethanol in this period. As a result, process steps from fermentation to dehydration as well as cogeneration section are not idle in the off-season. Although this alternative does not increase annual ethanol production, it presents as advantage lower investment on equipment, since the capacity of the sections that operate all year can be smaller. In order to store concentrated juice, it is necessary to invert sucrose to prevent sugars crystallization and degradation. Therefore, additional tanks for storage of the inverted and concentrated juice and more steam consumption for concentration are some disadvantages of this configuration.

On the other hand, processing a complementary feedstock in the same industrial facility would allow increasing ethanol and, in some cases, electricity production, thus increasing annual revenues. Nowadays, three alternative feedstocks are being considered to replace sugarcane during its off-season period: sweet sorghum, corn and, more recently, energy cane.

Sweet sorghum, similarly to sugarcane, contains readily fermentable sugars – such as sucrose and reducing sugars – and also generates bagasse that can be used as fuel in the cogeneration system to supply steam and electricity to the process. Thus, it may be processed using the existing industrial infrastructure of a sugarcane biorefinery (DURÃES, 2011). However, sweet sorghum presents a higher proportion of reducing sugars, aconitic acid and starch, when compared to sugarcane, which difficults sucrose crystallization required in the sugar production process (CUTZ; SANTANA, 2014).

Sweet sorghum is a short cycle culture (4 months) and can be utilized in rotation with other annual crops, and potentially, with sugarcane. For instance, sweet sorghum could be planted as a rotation culture or in land where sugarcane yields are limited due to marginal soils.

Regarding the agricultural machinery, the current belief is that sweet sorghum can be harvested, collected and transported with the existing sugarcane equipment fleet (SWAYZE, 2009). However, planting and cultural treatments may require a different structure as well as a technical team dedicated to sweet sorghum (SORDI, 2011). Therefore, adaptation of the machinery for an efficient harvesting, definition of a strategy for planting and advance on the learning curve are some challenges to be overcome with experience gathered each year (NOVACANA, 2013). In 2011, the first experience on industrial scale for production of ethanol from sweet sorghum in Brazil was reported (PORTO, 2011).

Cutz and Santana (2014) evaluated the use of sweet sorghum in Central America in sugarcane mills and concluded that its processing during off-season in sugarcane biorefineries improves profitability as both ethanol and electricity production increase.

Another alternative, already tested in industrial scale, is corn. For its processing to ethanol, an additional hydrolysis step to convert starch into fermentable sugars is required, which is associated to retrofitting costs. In order to adapt to Brazilian reality, instead of using natural gas and electricity, bagasse is stored to provide energy to the process. Usimat, the first Brazilian sugarcane mill to produce corn ethanol in a commercial scale, produced 7 million liters between the end of 2012 and beginning of 2013 (INFORMA ECONOMICS FNP, 2013).

Milanez et al. (2014), using the Virtual Sugarcane Biorefinery platform, assessed different integration scenarios of corn and sugarcane and showed that there is potential to increase in 10 % the amount of ethanol produced in Brazil without planting more sugarcane or building new mills; however better economic performance is achieved with low corn prices and high demand for animal feed (corn ethanol co-product) and, therefore, depends on regional factors.

More recently, energy cane, a cane selected to have more fibers than sugars, has been pointed out as a promising alternative feedstock. The high biomass productivity of energy cane reduces the need for land, requiring about half of the area to produce the same dry mass of sugarcane. Besides, this feedstock can be available all year-round, since fiber content does not vary during the year (MATSUOKA et al., 2014). Juice can be extracted from energy cane, probably with lower efficiency due to the higher fiber content, and bagasse can be used to increase electricity generation or as feedstock for 2G ethanol production.

The 2G ethanol production arises as another possibility for year-round operation, since lignocellulosic materials (such as sugarcane bagasse and straw) can be stored for off-season operation. However, significant investment on equipment is required for biochemical conversion of biomass to ethanol.

2.5. Biodigestion process

Biodigestion (or anaerobic digestion) is extensively used for the treatment of agricultural manures, sewage sludge, industrial food processing wastes, and for processing of the organic fraction of municipal solid waste. It is considered a mature technology, although with significant potential for increase in efficiency and productivity. In this sense, anaerobic digestion has been the subject of extensive research, for instance, process variations, including operation at mesophilic (37 °C) and thermophilic (55 °C) conditions, are optimized for different applications and feedstocks. (MURPHY; POWER, 2009).

Generally, biogas produced in anaerobic digestion plants is mainly composed of methane (CH_4) and carbon dioxide (CO_2) with smaller amounts of hydrogen sulphide (H_2S) and ammonia (NH_3). Trace amounts of hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), saturated or halogenated carbohydrates and oxygen (O_2) are occasionally present in the biogas. Usually, it is water saturated and may contain dust particles and siloxanes (IEA BIOENERGY, 2001).

Applications of biogas include mostly generation of heat and electricity. Boilers do not have a high gas quality requirement, but it is recommended to reduce the H_2S concentrations lower than 1000 ppm. Internal combustion engines have comparable requirements for gas quality as boilers except that the H_2S should be even lower to guarantee a reasonable operation time of the engine (IEA BIOENERGY, 2001). Biogas can be also upgraded to biomethane by removing CO_2 and H_2S, and injected into the natural gas grid or used as fuel in natural gas vehicles (IEA, 2011).

Biogas and biomethane can be stored and converted into electricity in high demand periods, or fed into the natural gas grid for use in open-cycle natural gas plants, allowing a rapid response to short-term variability in the power system and providing peak-load electricity (IEA, 2012).

Biodigestion can be applied as a treatment technology for vinasse (also called stillage), which is an aqueous residue from ethanol distillation process, produced in a proportion of approximately 13 L of vinasse for each liter of alcohol (SALOMON; LORA, 2009). The most common destination of this effluent is on soil as fertilizer – namely fertirrigation – for sugarcane cultivation because of its content of organic matter and nutrients (mainly potassium but also nitrogen and phosphorus) (MORAES et al., 2014). In São Paulo State, the application of vinasse is controlled by the amount of K_2O applied instead of controlling the application based on volume. Other Brazilian states are tending to adopt the same concept (MEYER et al., 2011). From an economic perspective, this application represents the least expensive and simplest solution for discharging this voluminous effluent based on Brazilian environmental legislation; however, there are uncertainties on environmental impacts even though it is allowed by law (MORAES et al., 2014). The nutrients contained in the vinasse – macro-nutrients (N, P, and K), micro-nutrients (Fe, Zn, Mn, Cu, and Mg), and nonessential metals – are generally conserved through anaerobic digestion, while the majority of the organic content is removed (WILKIE et al., 2000).

In this context, anaerobic digestion prior to fertirrigation has been considered an effective method for reducing COD (chemical oxygen demand) of vinasse and converting it to biogas, which is a readily usable fuel for the ethanol facility. Besides, sulfur can also removed from vinasse and recovered as a by-product (MORAES et al., 2015)

The chemical composition of vinasse depends on the characteristics of the soil, the variety of sugarcane, the period of the harvest and the industrial process used for the production of ethanol. Besides, COD of vinasse ranges from 15 to 33 g/L when the fermentation is carried out with sugarcane juice, 65 g/L when molasses are used and varies from 40 to 50 g/L using their mixture (SALOMON; LORA, 2009).

In a sugarcane mill, biogas can be burnt in the boilers (cogeneration system) or used in internal combustion engines. Alternatively, biogas can be upgraded to be sold as a natural gas substitute or used to partially replace diesel in the agricultural machinery (MORAES et al., 2014).

The latter is an important example of integration between agricultural and industrial sectors and presents as advantage the reduction of fossil energy use in the sugarcane chain.

In Brazil, the only vinasse biodigestion unit mentioned in the literature is located in the São Martinho mill, situated in São Paulo State. It consists on a 5000 m³ up-flow anaerobic sludge blanket (UASB), operated in thermophilic conditions, that produces biogas to provide energy for yeast drying (MORAES et al., 2015).

Additional concern related to vinasse generation is expected due to implementation of 2G process, due to increased volumes and characteristics that may differ from 1G vinasse. Moraes et al. (2015) observed that 2G vinasse presents higher organic matter content than the vinasse from 1G ethanol production, but has a similar BOD (biochemical oxygen demand) to COD ratio. In contrast, the content of nutrients and minerals, especially potassium, was found to be considerably lower for 2G vinasse. It is important to highlight that there is limited information on 2G vinasse available on the literature, especially on efficiencies for COD removal.

In 2G process, another liquid stream that stands out is the pentoses liquor obtained during the pretreatment of sugarcane bagasse and straw. Although the conversion of pentoses to ethanol is preferred, some obstacles may prevent its industrial implementation in the short term. Since conventional yeast is not able to ferment pentoses, the use of genetically modified organisms (GMO) has been reported (KUMAR et al., 2009; GÍRIO et al., 2010). The challenge is to develop robust strains with ability to produce ethanol from all the sugars available in lignocellulose hydrolysates with maximum ethanol yields/productivities and minimum cultivation times (CHANDEL et al., 2011). Therefore, pentoses liquor need an appropriate destination to avoid environmental damage while conversion to ethanol or other products is not technologically feasible on a full scale (MORAES et al., 2015).

The composition of the pentoses liquor generated during the 2G process is not precisely defined, because different technologies can be applied to the pretreatment of sugarcane lignocellulosic materials. In addition, there is no available literature on operation of anaerobic reactor treating the resultant pentoses liquor (MORAES et al., 2015).

Macrelli et al. (2012) performed experimental trials to obtain data for the biogas potential from vinasse and pentoses liquor from bagasse. The final methane yield was 0.112 and 0.127 $gCH_4/gCOD$ for the vinasse and pentoses liquor, respectively. The authors considered only pentoses liquor biodigestion in their evaluation, since it presents a better relation between capital cost and methane production capacity.

2.6. Biorefinery simulation and economic evaluation

The biorefinery concept is analogous to the basic concept of conventional oil refineries: to produce a variety of fuels and other products from a certain feedstock. Biorefineries can potentially make use of a broader variety of biomass feedstocks and allow for a more efficient use of resources, providing a variety of products to different markets and sectors (IEA, 2011).

First generation ethanol facilities can already be considered biorefinery models. Sugarcane biorefineries can produce ethanol, sugar and electricity, while corn ethanol production includes dried distiller's grains with solubles (DDGS) and fructose as co-products, which heavily influence overall economic and environmental efficiency of this process (IEA, 2011).

In the second generation process, in addition to ethanol production, monosaccharides (e.g., glucose and xylose) obtained after biomass hydrolysis can be converted, via fermentation or chemical synthesis, to building block chemicals, which in turn can be used in the production of numerous value-added chemicals (CHERUBINI, 2010).

Taking into consideration the complexity of the biorefineries – regarding technological routes, product portfolio and biomass source – process simulation can be used to evaluate alternative configurations in a relatively fast manner, allowing the comparison of different process configurations and their impacts on the entire production process, which would be much harder to achieve in an experimental scale (DIAS et al., 2014).

Several works based on process simulation using the commercial software Aspen Plus® and biorefinery evaluation are available in the literature. For instance, a series of reports (ADEN et al., 2002; HUMBIRD et al., 2011) on techno-economic feasibility of 2G ethanol production from biochemical conversion of lignocellulosic biomass have been published by U.S.

National Renewable Energy Laboratory (NREL). The process design consisted on dilute-acid pretreatment and enzymatic hydrolysis of corn stover. Based on experimental data, obtained in the laboratory or pilot plant, process simulations were carried out, including not only second generation process steps, but also downstream process, cogeneration system and wastewater treatment. Process simulations allowed obtaining mass and energy balances of the entire plant as well as provided information for equipment sizing and economic feasibility assessment. These reports presented the evolution of minimum ethanol selling price with the advances and deeper understanding on 2G process along time, becoming a reference for both industrial and academic sectors.

Alzate and Toro (2006) investigated different flowsheet combinations (e.g., different pretreatment processes, fermentation configurations and ethanol separation technologies) for the biotechnological production of ethanol from wood chips. Process simulation was employed to evaluate the energy consumption (both thermal and electric) in the production of ethanol. The results demonstrated that the thermal energy required for the production of biomass ethanol could be balanced by the energy generated in the same process (e.g. combustion of lignin and biogas).

Barta et al. (2010) simulated and evaluated, from a techno-economic perspective, an on-site cellulase enzyme production integrated to a softwood-to-ethanol process. The effect of varying the carbon source (pretreated liquid fraction, slurry, and molasses) for enzyme production was investigated. Capital cost represented from 60 to 78 % of the enzyme production costs and the lowest minimum ethanol selling price was obtained in the scenarios using pretreated liquid fraction supplemented with molasses. The amount of C6 sugars consumed as carbon source was found to be an important factor, since it decreases the overall ethanol yield.

Dias (2011) performed a techno-economic assessment of 2G ethanol production from sugarcane residues (bagasse and straw), including different pretreatment methods, conditions for enzymatic hydrolysis and pentoses destination. In the integration to first generation, reduction on steam consumption as well as the use of sugarcane straw was found to be important to increase lignocellulose availability for second generation process.

Palacios-Bereche (2011) integrated a 2G process into a 1G ethanol production plant. The author employed the Pinch-Point method to perform the thermal integration of the system.

Increase on ethanol production in the conventional configuration was less than 10 %; after thermal integration and consideration of a membrane system for glucose concentration, the increase on ethanol production achieved 22.4 %.

Albarelli (2013) simulated and evaluated the integration of second generation process into autonomous and annexed plants. Sugar production presented a positive impact on economic feasibility, showing the importance of product diversification. In addition, the use of bagasse and bagasse fine fraction – composed by parenchyma cells (fraction-P) – for production of 2G ethanol were investigated. The latter was found to be more advantageous in terms of electricity generation, 2G ethanol production (per mass of lignocellulosic material treated) and from an economic perspective.

Macrelli (2014) evaluated different configurations for 2G integrated to a 1G ethanol plant. Simultaneous saccharification and fermentation (SSF) and time-separated hydrolysis and fermentation (tSHF) were investigated, as well as different destinations for pentoses (biodigestion and fermentation). The tSHF configuration and pentoses fermentation showed higher potential for reduction on minimum ethanol selling price.

In order to assess the development level of different technologies for sugarcane processing, the Brazilian Bioethanol Science and Technology Laboratory (CTBE) has developed the Virtual Sugarcane Biorefinery (VSB). The VSB is a simulation platform that allows evaluation of the integration of new technologies (for instance, cellulosic ethanol and other products from the green chemistry in the biorefinery concept) with the technologies practiced nowadays considering the entire sugarcane production chain: agricultural, transport, industrial and usage sectors. In addition, the main objective of the VSB is to compare and evaluate the economic, social and environmental impacts of different alternatives (CTBE, 2012).

Within the biorefinery concept, studies using the VSB have focused on the integration of 1G ethanol production to other routes. Some examples are: integration of 2G process (DIAS et al., 2012b), integration of butanol production using acetone–butanol–ethanol (ABE) fermentation (MARIANO et al., 2013a,b) and catalytic routes (DIAS et al., 2014; PEREIRA et al., 2014) as well as some specific analyses in process steps, such as cogeneration (DIAS et al., 2013) and fermentation (DIAS et al., 2012c).

3. Methodology

In this thesis, several process configurations were simulated and evaluated from a techno-economic standpoint. In this chapter, general methodology and main assumptions are presented. Further details for each study are presented in the following chapters along with scenarios description and results.

Techno-economic assessment was carried out using the Virtual Sugarcane Biorefinery framework described as follows.

3.1. The Virtual Sugarcane Biorefinery

The Virtual Sugarcane Biorefinery (VSB) is a tool that integrates different computer platforms such as Aspen Plus®, SimaPro® and electronic spreadsheets for integrated technical, economic, social and environmental assessments. In order to allow an integrated and complete evaluation, the VSB includes models for the entire sugarcane chain: agricultural, industrial and usage sectors (CTBE, 2012).

For the agricultural sector, the “Canasoft”, a spreadsheet model developed by CTBE, is used to calculate sugarcane production cost and provide information for life cycle assessment. This model includes a detailed description and data of the main operations of the sugarcane production (pre-planting operations, soil preparation, planting, cultivation, harvesting and sugarcane transport). This model can be adapted to include other biomasses; corn, sweet sorghum, energy cane are some examples already evaluated.

For the industrial sector, the software Aspen Plus® is used to perform mass and energy balances. This simulator contains a comprehensive library of components, properties and unit operation models as well as several thermodynamic packages.

For the usage sector, another model is being developed to evaluate the operations of commercialization and use of the different biorefinery products. At this initial stage, data related to ethanol use in vehicles (such as emission factors) are being introduced into the model.

The use of these modeling and simulation tools provides information for the sustainability assessment. In order to evaluate economic, environmental and social impacts, the following methodology was defined in the VSB platform:

- Economic analysis: estimation of capital investment cost, calculation of internal rate of return (IRR), net present value (NPV), production costs, among other parameters.
- Environmental analysis: evaluation of greenhouse gas emissions, energy balance (relation between the renewable energy produced and the fossil energy consumed), water consumption, land use changes and other environmental impacts included in the Life Cycle Assessment (LCA) such as acidification, nitrification, eutrophication and human toxicity.
- Social analysis: estimation of local impacts derived from the automation, plant scale, agricultural sector mechanization, among others, on the number and quality of created jobs (income and education level). The methodology to compare different alternatives, especially for those still in development, is under construction.

In addition to ethanol, sugar and bioelectricity – produced in the 1G process – other products, such as those derived from thermochemical conversion, sugarchemistry and alcoholchemistry routes, as well as other feedstocks may be considered in the assessment.

In order to include a new route or technology in the VSB, it is necessary to gather all the data required – e.g., process configuration, inputs used, operational conditions, yields – for mass and energy balances (from literature, experimental data or consultation with specialists) and to include new components and unit operations into the existing standard flowsheet to represent the alternative to be simulated. Besides, investment on equipment and market prices for feedstock, inputs and products are necessary to perform economic evaluation.

The studies presented in this thesis focused on simulation of industrial sector and economic analysis. The methodology adopted is detailed in the following sections.

3.2. Process Simulation

The software Aspen Plus® was employed to represent industrial sector in sugarcane chain. As presented in the Chapter 2, several works available in the literature were based on the use of this commercial simulator.

Hierarchy blocks were used to organize process flowsheet, since sugarcane processing includes several unit operations. As an example, the integrated 1G2G process flowsheet is shown in Figure 5. At a first level, it is possible to identify the main process steps: sugarcane preparation and extraction (PREP-EXT), ethanol production (ETHANOL), second generation process (2G) and CHP unit.

Different thermodynamic models were used according to the section of the plant. In the early stages of processing (previous to fermentation), sugar processing and 2G plant, the NRTL-RK (NRTL – Non Random Two Liquid for liquid phase and RK - Redlich-Kwong for vapor phase) model was adopted to represent sugar containing streams (DIAS, 2011). For fermentation, distillation and dehydration, the NRTL-HOC (HOC - Hayden O' Connell) was employed due to the presence of acetic acid and other carboxylic acids produced in the fermentation to account for the nonideality of the vapor (JUNQUEIRA, 2010). In the cogeneration system, RKS-BM model (RKS - Redlich-Kwong-Soave and BM - Boston-Mathias alpha function) was chosen to represent the high temperature gases, while STEAMNBS was used for calculation of steam thermodynamic properties (DIAS, 2011).

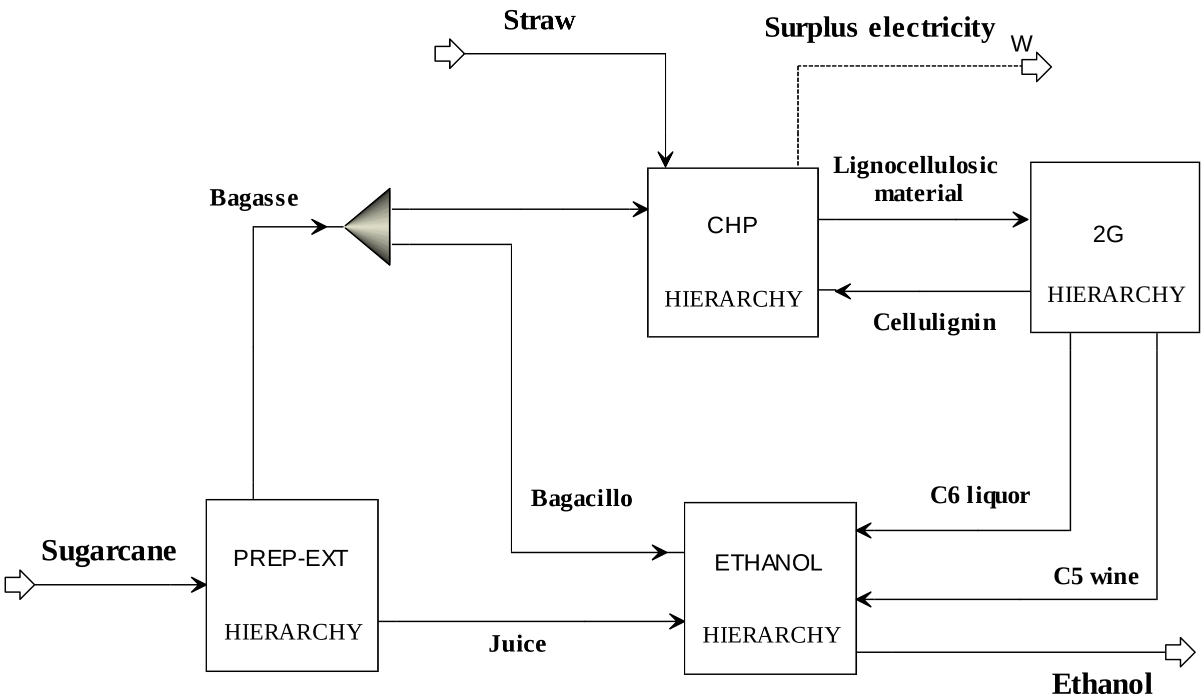

Figure 5. Process flowsheet for integrated 1G2G ethanol production.

3.2.1. Simulation of 1G process

A typical 1G ethanol production process from sugarcane is comprised by the following main steps:

- Sugarcane and straw reception;
- Sugarcane cleaning, preparation and sugar extraction;
- Juice treatment and concentration;
- Fermentation;
- Distillation and ethanol dehydration;
- Sugar crystallization and drying (only in annexed plants);
- Cogeneration system.

Process flowsheet, operational conditions and efficiencies for each unit operation were gathered from literature, visit to industrial plants and consultation with specialists in order to represent Brazilian sugarcane biorefineries as close as possible.

Sugarcane and straw reception

Sugarcane quality varies considerably according to time of planting, type of soil, climate conditions, etc. The composition of sugarcane stalks considered in the VSB is presented in Table 1. A sugarcane industrial facility processing 2 million metric tons of sugarcane (TC) per year and effective operation period of 200 days/year was assumed, corresponding to about 417 TC/h.

Table 1. Composition of the sugarcane adopted in the Virtual Sugarcane Biorefinery (CTBE, 2012).

Component	**Content (wt%) in the sugarcane stalks**	**Content (wt%) in the sugarcane received in the mill**
Organic acids	0.56	0.56
Reducing sugars	0.60	0.60
Minerals	0.20	0.20
Salts	1.31	1.30
Phosphate	0.03	0.03
Dirt (soil)	0.00	0.60
Sucrose	14.00	13.92
Water	70.29	69.87
Fibers	13.00	12.92
- *Cellulose*	*5.99*	*5.95*
- *Hemicellulose* [a]	*3.54*	*3.52*
- *Lignin*	*3.21*	*3.19*
- *Ash*	*0.27*	*0.27*

[a] Hemicellulose fraction is composed by xylan and acetyl group in a proportion of 10 : 1.

In addition to the stalks, the sugarcane plant also produces straw (sugarcane tops and leaves) in a proportion of approximately 140 kg of straw (dry basis) per ton of sugarcane stalks. Sugarcane straw composition, given in Table 2, was based on bagasse composition (sugarcane fibers). Straw recovery was assumed to be through baling in a proportion of 50% of that produced in the field.

Table 2. Composition of the sugarcane straw adopted in the simulations (adapted from CTBE, 2012).

Component	**Composition (% wt, dry basis)**
Cellulose	46.05
Hemicellulose [a]	27.20
Lignin	24.67
Ash (minerals, salts and dirt)	2.08

[a] Hemicellulose fraction is composed by xylan and acetyl group in a proportion of 10 : 1.

Sugarcane cleaning, preparation and sugar extraction;

After reception, sugarcane is cleaned to remove most of the dirt carried along from the field. A dry cleaning system was considered, since mechanically harvested sugarcane (chopped) would present high sugar losses if washed. Due to the banishment of burning practices, increase on mechanization of agricultural operations has occurred in the last years. Efficiency of dirt removal of 70 % and 0.5 % sugarcane losses was assumed (DIAS, 2011).

Prior to sugar extraction, sugarcane is fed to a preparation system – comprised by knives, shredders, hammers, etc – to open the cell structure and enhance sugar extraction. Since only physical changes occur, this step was not modeled in the simulation, only electricity demand is included in the overall consumption of the plant.

Milling operation is considered for sugar extraction, using countercurrent water (imbibition) to improve sugars recovery, separating sugarcane juice from bagasse. Sugarcane juice is a solution of water, sucrose, reducing sugars, other soluble solids, dirt and fiber particles. A screen is used to retain solid particles (mostly fibers) from the juice; these fibers are recycled to the mills for further recovery of sugars, while the juice is sent to treatment. Main parameters adopted in the simulation are shown in Table 3.

Table 3. Main parameters adopted in the simulation for sugar extraction (CTBE, 2012).

Parameter	**Value**
Amount of imbibition water (related to amount of sugarcane)	28 %
Efficiency of sugar extraction in the mills	96 %
Bagasse moisture	50 %
Efficiency of dirt and bagasse removal in the screen	65 %

The process flowsheet including dry cleaning, milling and screen is depicted on Figure 6. These operations were represented by component separators (Sep model [1]), which are based on separation efficiency. Aspen Plus® library has models that would represent these operations (e.g. Screen model[2]), but some specific parameters, such as particle size distribution (not available at this time), are required. Besides, although it is a more detailed model, it would not add relevant information for simulation purposes.

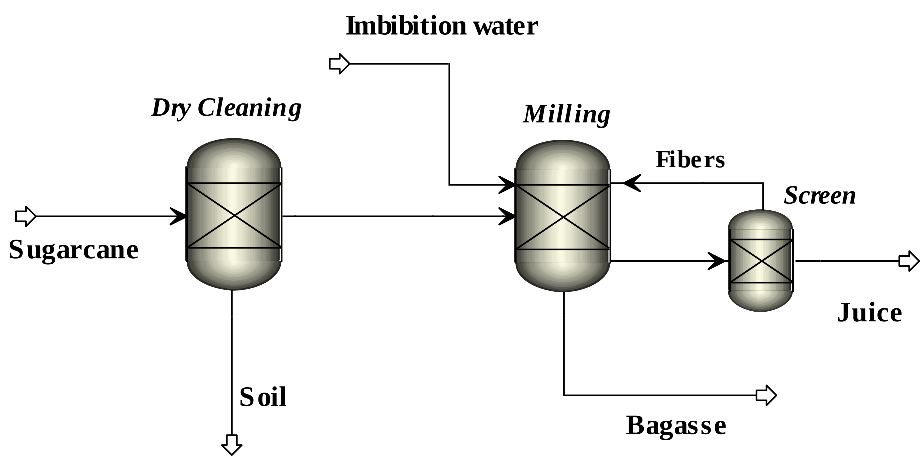

Figure 6. Process flowsheet for sugarcane cleaning and extraction.

[1] Sep is an Aspen Plus® model that separates inlet stream components into multiple outlet streams, based on specified flows or split fractions for each component. It is used when the details of the separation are unknown or unimportant.

[2] Screen simulates the separation of solid particles in a mixture based on the sizes of particles and screen openings specified by user.

Juice treatment and concentration

The presence of impurities in the juice may affect fermentation to ethanol and sugar crystallization. For this reason, a series of operations are carried out to remove impurities and produce clarified juice. First, juice is heated to 70 ºC, using thermal integration with broth (the concentrated juice that will feed fermentation). Phosphoric acid and lime are added and then juice undergoes a second heating stage to achieve 105 ºC.

The heated juice is flashed to remove non-condensable gases, receives flocculant (such as polyacrylamide) and is pumped to a settler; slurry, which contains most of the impurities, settles down in the bottom of the vessel and clarified juice is obtained in the upper part.

The slurry is sent to a filter along with bagacillo (bagasse fines) and water so that part of the remainder sugars can be recovered. The obtained filter cake is sent to the field for nutrients recycle. The filtrate is mixed with the juice prior to the second heating stage.

The clarified juice is fed to screens for further removal of solid particles, followed by evaporation to achieve the concentration needed in the next step. For ethanol production, in an autonomous plant, there is only one stage of evaporation. In an annexed plant, a 5-stage multiple effect evaporator is usually employed to produce syrup (65 wt% soluble solids) for sugar production, while molasses (by-product of sugar production) are added to increase juice concentration for ethanol production.

Process flowsheet for juice treatment and concentration are presented in Figure 7 and Figure 8, respectively. Liming was modeled by a stoichiometric reactor (RStoic model[3]); filter, settler and screen were represented as component separators; flash vessel and evaporators by a

[3] RStoic is an Aspen Plus® model where stoichiometric reactions with specified reaction extent or conversion are specified. It is used when reaction kinetics are unknown or unimportant.

two-outlet flash (Flash2 model[4]); and heating operations through heat exchange models (Heater[5] and HeatX[6]). Auxiliary equipments such as mixers, splits, valves and pumps were also included. Proportion of inputs addition and efficiencies on each step are shown in Table 4.

Table 4. Main parameters adopted in the simulation of the sugarcane juice treatment operations (CTBE, 2012).

Parameter	**Value**
Phosphate content of the juice after phosphoric acid addition	250 ppm
Amount of lime added in liming (ethanol/sugar production)	0.6/1.0 kg CaO/TC
Amount of flocculant polymer	2.5 g/TC
Efficiency of settling of insoluble solids	99.7 %
Amount of wash water related to filter cake	150 %
Bagacillo added in the filter	0.6 t/100 TC
Solids retention in the filter	65 %
Filter cake sucrose content	1 %
Amount of filter cake produced (ethanol/ sugar production)	25/45 kg/TC
Efficiency of removal of insoluble solids in the screen	65 %

[4] Flash2 is an Aspen Plus® model used to separate the feed into two outlet streams, using rigorous vapor-liquid equilibrium.

[5] Heater model can represent heating and cooling operation through specification of thermal and phase conditions of an outlet stream.

[6] HeatX calculates the heat exchange between two streams.

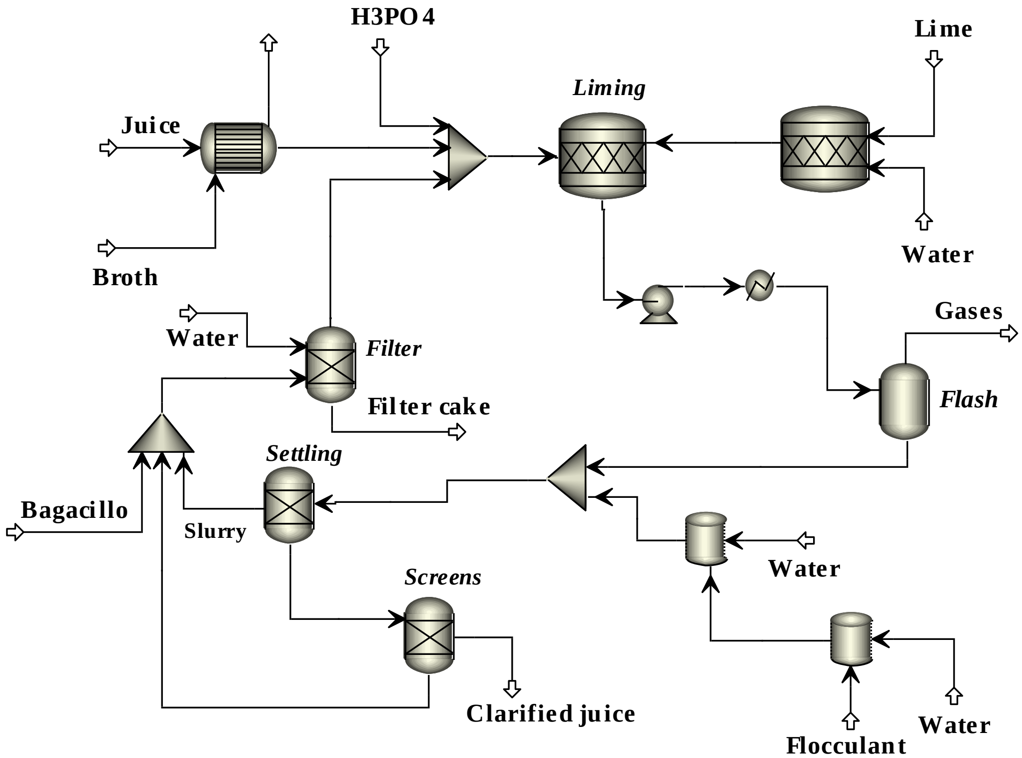

Figure 7. Process flowsheet for juice treatment.

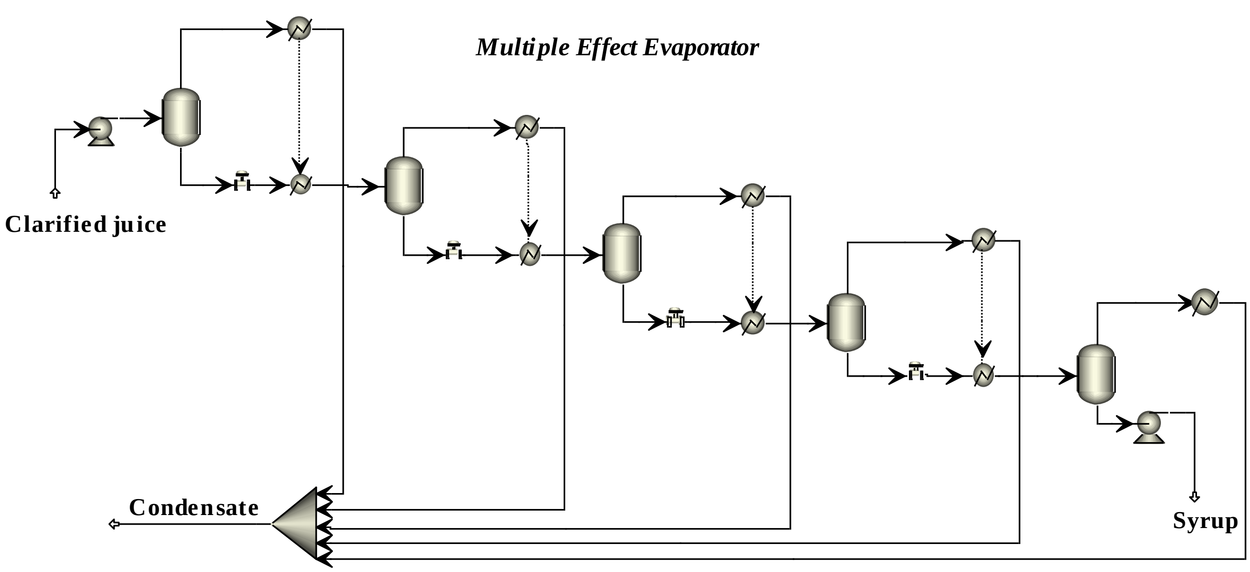

Figure 8. Process flowsheet of juice concentration for sugar production.

Fermentation

A fed-batch fermentation process with cell recycle was assumed. Broth is cooled to achieve fermentation temperature (33 ºC) and is sent to the reactor along with yeast cells. A stoichiometric reactor is employed to represent the fermentation reactor, considering the following reactions for sucrose inversion (reaction 1) and production of ethanol (reaction 2), cells growth (reaction 3) and formation of by-products (reactions 4, 5, 6 and 7). The stoichiometry of reactions was not based on metabolic reactions, which are more complex and not always available, but defined based on mass balance. As a simplification, reducing sugars (fructose and glucose) were represented only by glucose.

$$Sucrose + H_2O \rightarrow 2\ Glucose \quad (1)$$

$$Glucose \rightarrow 2\ Ethanol + 2\ CO_2 \quad (2)$$

$$3.2618\ Glucose + 2.8469\ NH_4OH + 2.1352\ CO_2 \rightarrow 1.0359\ Acetic\ acid + 6.9454\ H_2O + 19.6342\ Yeast \quad (3)$$

$$0.7630\ Glucose \rightarrow 0.7630\ Isobutanol + 1.5260\ CO_2 + 0.7630\ H_2O \quad (4)$$

$$0.6107\ Glucose + 0.5236\ H_2O \rightarrow 0.5234\ CO_2 + 1.047\ Glycerol \quad (5)$$

$$Glucose \rightarrow 3\ Acetic\ acid \quad (6)$$

$$0.8271\ Glucose \rightarrow 0.6617\ Isoamyl\ alcohol + 1.6542\ CO_2 + 0.9927\ H_2O \quad (7)$$

The fermentation product, known as wine, is centrifuged aiming the separation of yeast cells. Separation efficiency of cells and other components were defined in a component separator. The yeast cells are treated with sulfuric acid and diluted with water before returning to the fermentation reactor. Wine, with ethanol concentration around 8.5 ºGL (% v/v), is sent to a set of distillation columns.

During fermentation, a large amount of CO_2 is formed and part of the produced ethanol is dragged with the gases. An absorption column (Radfrac model[7]) is used to recover ethanol using

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[7] RadFrac model performs rigorous rating and design calculations for single columns. Ordinary distillation, absorbers, strippers, extractive and azeotropic distillations are some possible applications.

water as entrainer; an alcoholic solution (around 3 wt% ethanol) is generated and mixed to wine prior to distillation.

Process flowsheet and the main parameters adopted in the simulation of the fermentation process are shown in Figure 9 and Table 5.

Table 5. Main parameters adopted in the simulation of the fermentation process (CTBE, 2012).

Parameter	**Value**
Fraction of the reactor fed with yeast suspension	25 wt%
Conversion of sugars to ethanol (autonomous/annexed plant)[a]	90 %/89.5 %
Efficiency of solids retention in the centrifuges	99 %
Ethanol content of the yeast concentrated solution obtained in the centrifuges	6.5 %
Sulphuric acid addition in yeast treatment (on 100 % basis)	5 g/L ethanol

[a] Due to the presence of inhibitory compounds in the molasses, fermentation yield for annexed plant is lower than that of autonomous distillery.

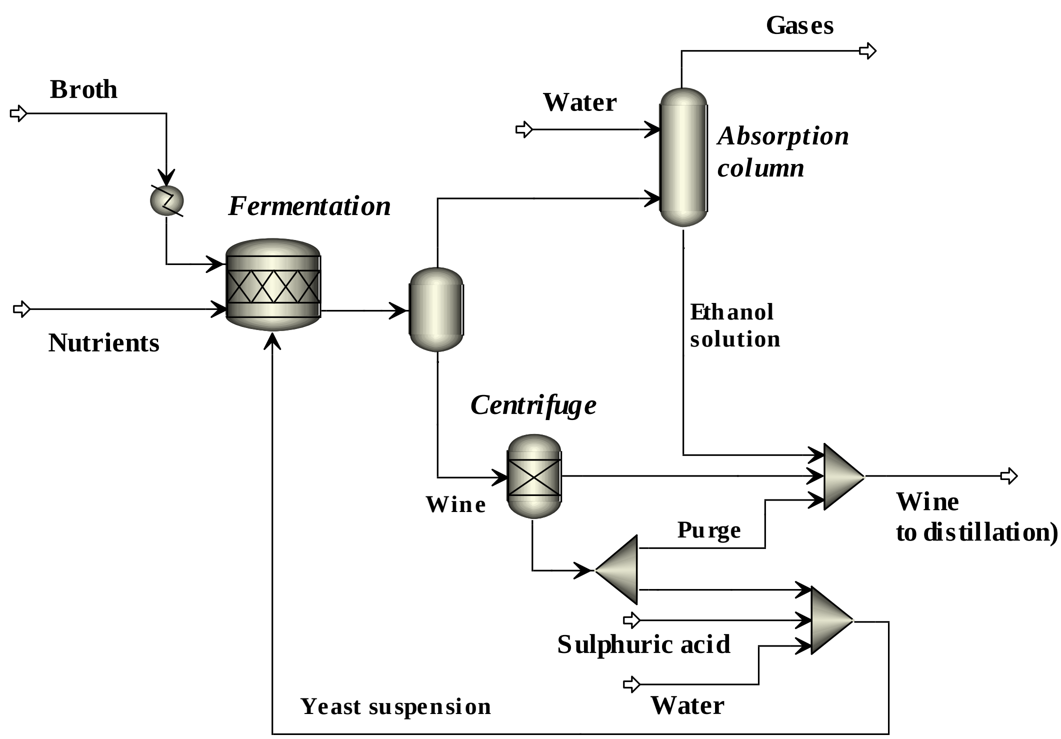

Figure 9. Process flowsheet for fermentation and cells treatment.

Distillation and ethanol dehydration

The scheme considered for distillation and dehydration is depicted in Figure 10. Wine is heated up to 82 ºC prior to distillation. Usual configuration of distillation section includes five columns. The first set of columns (usually named A, A1 and D) originates vinasse – an aqueous residue produced in the bottom – and two alcoholic streams, called phlegm, with a concentration around 50 ºGL and, in the top, a 2^{nd} grade alcohol stream concentrates the most volatile compounds.

The phlegms follow to the second set of columns (known as B and B1), where another aqueous stream is produced in the bottom (phlegmasse) and ethanol is recovered in the upper part of the column as hydrous ethanol (93 wt%). Fusel oil, containing most of the higher alcohols, is obtained as a side withdrawal in column B.

Distillation columns were represented in the simulator by RadFrac model and the input specifications were defined in a way that ethanol concentration in vinasse and phlegmasse were lower than 200 ppm and hydrous ethanol grade (93 wt%) was achieved.

For ethanol dehydration, most of sugarcane facilities still employ azeotropic distillation with cyclohexane, which requires a large amount of steam (around 2 kg/L of anhydrous ethanol). This process employs two distillation columns, in the first one a ternary heterogeneous azeotrope is recovered at the top and sent to a decanter, where two liquid streams are obtained. The aqueous phase is sent to a second column where pure water is obtained in the bottom and the top stream, along with the organic phase (rich in cyclohexane), is recycled to the first column. Anhydrous ethanol is produced in the bottom of the first column. Simulation of the azeotropic distillation process is often complex mainly because of the formation of a second liquid phase inside the azeotropic column (JUNQUEIRA, 2010). A simplified model based on a component separator and steam demand was included in the simulation. Product specification of anhydrous ethanol was set to 99.6 wt%.

As an alternative dehydration method, adsorption with molecular sieves was considered in the optimized scenarios aiming at reducing steam consumption (0.6 kg/L of anhydrous ethanol). In this process, besides anhydrous ethanol, an alcoholic stream (around 70 % ethanol) is generated and is recycled back to the distillation columns. As this process is a transient operation, it was also represented by a component separator in Aspen Plus®.

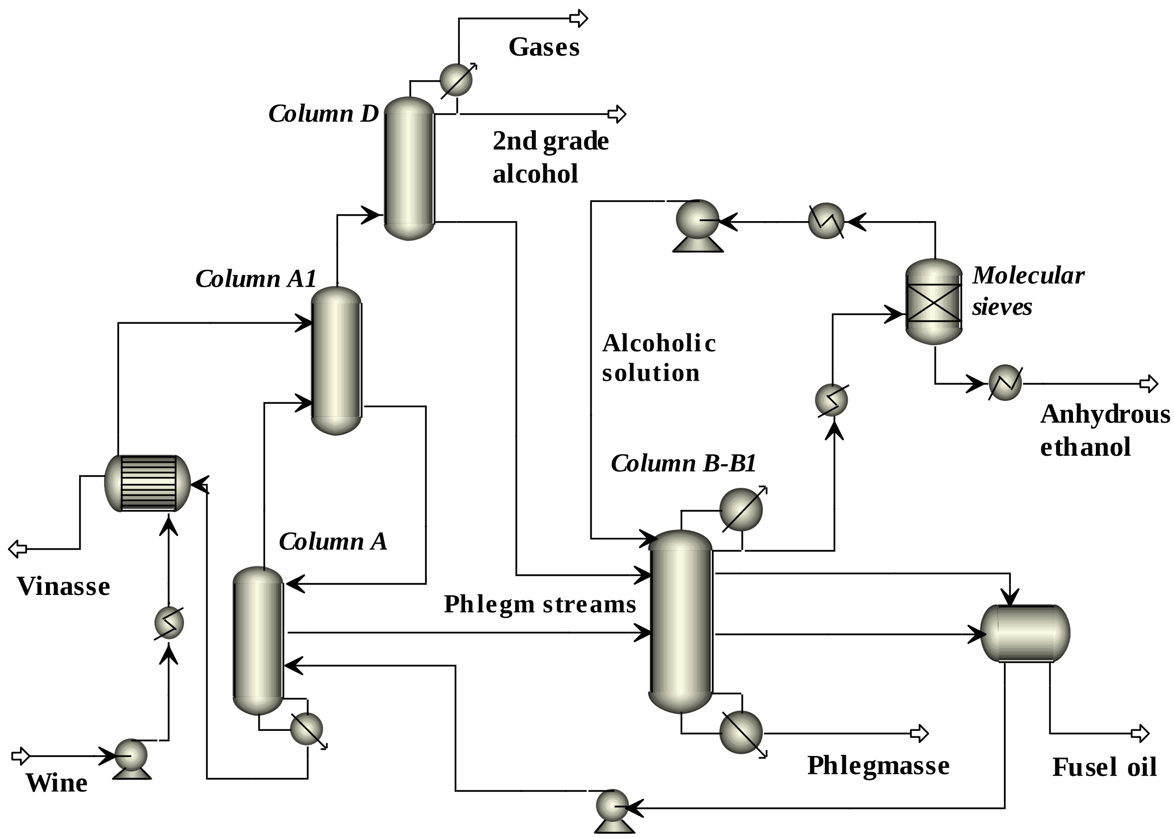

Figure 10. Process flowsheet for distillation and ethanol dehydration using molecular sieves.

<u>Sugar crystallization and drying</u>

Process flowsheet for sugar crystallization and drying, additional steps required for sugar production, is shown in Figure 11.

Syrup from the evaporators is sent to vacuum pans and crystallizers (represented by a two-outlet flash model), where evaporation and sucrose precipitation ocurr, generating a mixture of sugar crystals and liquid denominated massecuite. Crystals are separated using centrifuge, which was represented by a component separator. The liquid fraction, called 'A' molasses, is sent to another set of vacuum pans and crystallizers in order to recover more sucrose, producing final molasses. The crystal fraction from 'B' massecuite is dissolved and recycled mixed to the syrup.

Crystals obtained from ‘A’ massecuite are dried and cooled for storage as the final product. Sugar purity and moisture specifications of 99.6 % and 0.1 % (mass basis), respectively, were assumed. Overall sugars recovery as final product is 76.5 %. Final molasses, with a total reducing sugars content of approximately 60 %, are destined to ethanol production (CTBE, 2012).

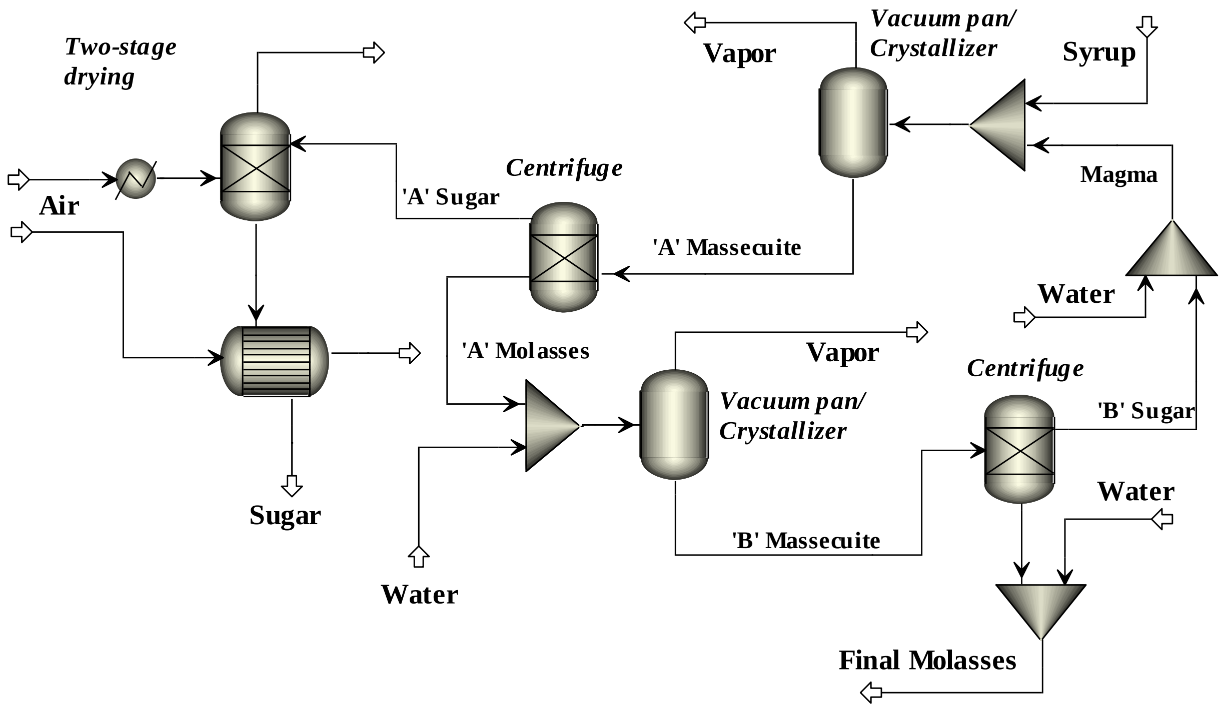

Figure 11. Process flowsheet for sugar crystallization and drying.

<u>Cogeneration system</u>

Cogeneration system or combined heat and power (CHP) produces all the thermal, mechanical and electrical energy required in the sugarcane processing, commonly using bagasse as fuel. Traditional sugarcane mills have low efficiency systems, but more efficient systems have been gaining ground with the possibility of selling electricity to the grid.

In order to represent the average configuration of Brazilian sugarcane mills, referred in this work as basic configuration, a low efficiency 22 bar / 300 °C boiler system was considered. Alternatively, in the optimized configuration, a 65 bar / 485 °C boiler system was considered to represent the new and optimized CHP units. In order to increase electricity production, straw recovery was assumed in some scenarios for use as complementary fuel in efficient cogeneration systems.

Regardless of the boiler pressure, this operation was represented by a stoichiometric model reactor to simulate combustion reactions and by a HeatX model for heat exchange between hot gases generated after combustion and pressurized water, resulting in high pressure steam (22 bar and 65 bar, depending on boiler pressure). Conversion of the combustion reactions was set as 100 %; the loss of a fraction of the hot gases was varied to achieve boiler efficiency for each system (see Table 6). Based on the enthalpy of combustion for each component, sugarcane bagasse lower heating value (LHV) was calculated as 7.5 MJ/kg (50% moisture) and 14.9 MJ/kg for straw (15 % moisture).

Table 6. Main parameters of the combined heat and power system (DIAS et al., 2012).

Parameter	**Value**
22 bar boiler system	
Boiler efficiency (LHV[a] basis)	75 %
Gases outlet temperature	170 °C
Steam temperature	300 °C
Turbine isentropic efficiency	72 %
Direct drives isentropic efficiency	55 %
Generator efficiency	98 %
Electric energy demand of the process (with direct drivers)	12 kWh/TC
Mechanical energy demand of the process (with direct drivers)	16 kWh/TC
Process steam pressure (bar)	2.5
65 bar boiler system	
Boiler efficiency (LHV basis)	87.7 %
Gases outlet temperature	160 °C
Steam temperature	485 °C
Turbine isentropic efficiency	85 %
Generator efficiency	98 %
Electric energy demand of the process (with electric drivers)	30 kWh/TC
Process steam pressure (bar)	2.5 and 6.0
General Parameters	
Condensate losses	5 %
Fraction of bagasse for start-ups of the plant	5 %

The high pressure steam is expanded in a series of turbines (Compr model[8]) that correspond to extraction of steam in different pressures to supply the process and generate electricity. In the 22 bar boiler system, low efficiency steam turbines as mechanical (direct) drivers were assumed.

In the optimized scenarios, electrified drivers were considered for mills and other equipment, since they are more energy efficient than direct drivers. In addition, a turbine with final condensing stage is used to further expand the amount of steam that exceeds process demand until 0.11 bar, increasing electricity generation, since all bagasse/straw are burnt. Process flowsheet for this configuration is presented in Figure 12.

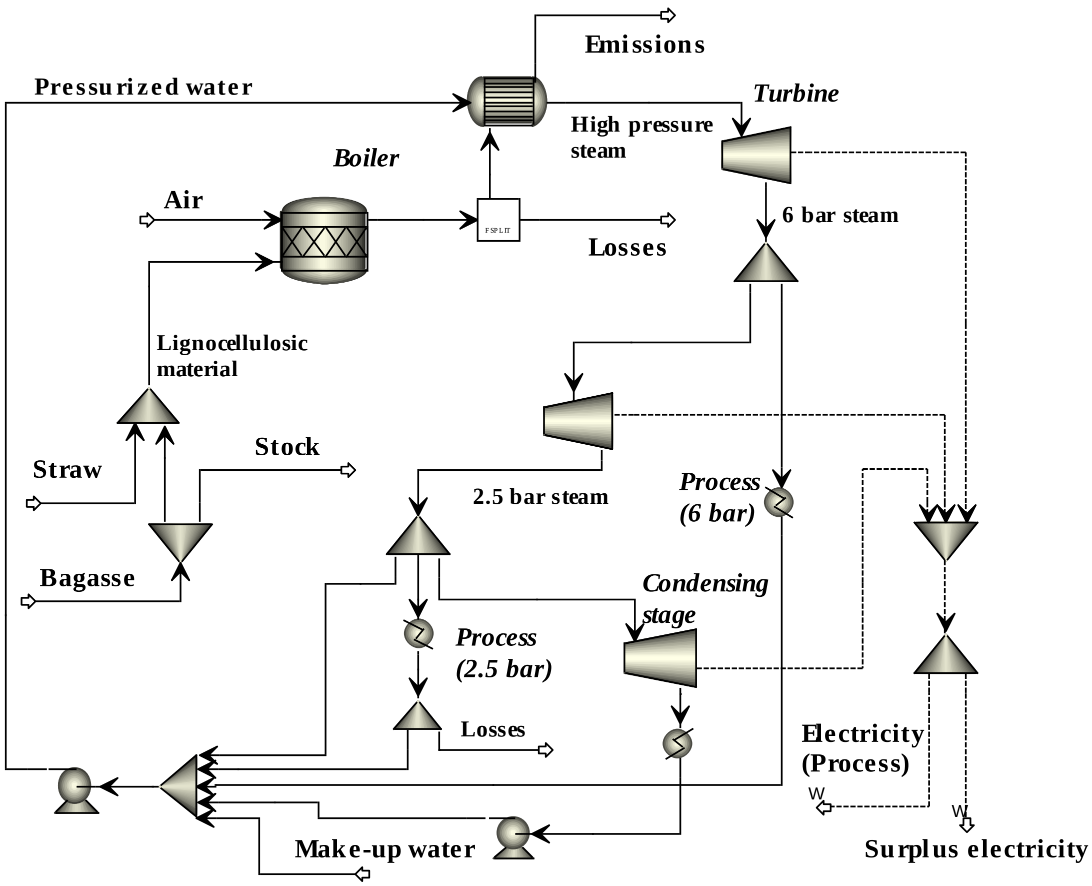

Figure 12. Combined heat and power generation with extraction-condensing turbine.

[8] Compr is an Aspen Plus® model that represents either a compressor or turbine. In the simulation, outlet turbine pressure and isentropic efficiency are defined; as a result the power is calculated.

3.2.2. Simulation of 2G process and 1G2G integration

In order to be used as feedstock for ethanol production, lignocellulosic materials such as sugarcane bagasse and straw must undergo a pretreatment process through which the hemicellulose (xylan and acetyl group) is removed and the cellulose becomes more accessible to enzymatic attack during hydrolysis. Xylan is solubilized in C5 monomers and oligomers (reactions 8 and 9) as well as degradation product (reaction 10). The proportion between these products is dependent on the pretreatment conditions (pressure, temperature, pH, reaction time). Acetic acid formation also occurs due to acetyl group solubilization (reaction 11). The process is designed in a way to minimize solubilization of cellulose (reactions 12, 13 and 14) and lignin (reaction 15). Although degradation products are formed as a consequence of sugars dehydration, reactions were inserted in such way that conversion would be calculated based on carbohydrate polymers.

$$(Xylan)_n + n\,H_2O \rightarrow n\,Xylose \qquad (8)$$

$$(Xylan)_n + n\,H_2O \rightarrow n\,Xylose\ Oligomers \qquad (9)$$

$$(Xylan)_n \rightarrow n\,Furfural + \ 2n\,H_2O \qquad (10)$$

$$Acetil\ group \rightarrow Acetic\ acid \qquad (11)$$

$$(Cellulose)_n + \ n\,H_2O \rightarrow n\,Glucose \qquad (12)$$

$$(Cellulose)_n + \ n\,H_2O \rightarrow n\,Glucose\ Oligomers \qquad (13)$$

$$(Cellulose)_n \rightarrow Hydroxymethylfurfural + 2n\,H_2O \qquad (14)$$

$$(Lignin)_n \rightarrow n\,Soluble\ lignin \qquad (15)$$

Note: Xylan, cellulose and lignin were inserted in Aspen Plus® in a monomeric form, thus “n” was considered equal to 1.

The pretreated solids are separated from the obtained pentoses liquor; pentoses are either fermented into ethanol (reaction 16) or biodigested (producing biogas for the cogeneration system), depending on the configuration.

$$3\ Xylose \rightarrow 5\ Ethanol + 5\ CO_2 \qquad (16)$$

The solid fraction is sent to enzymatic hydrolysis, where residual hemicellulose and cellulose are hydrolyzed (reactions 8 and 12, respectively) and the remaining acetyl group and lignin are solubilized (reactions 11 and 15, respectively). The material produced is separated in two fractions, the hydrolyzed liquor, rich in glucose, and the unreacted solids (residual cellulignin).

In the integrated 1G2G process, the hydrolyzed liquor (or C6 liquor) is mixed with sugarcane juice; thus, concentration, fermentation, distillation and dehydration operations are shared between both processes.

The residual cellulignin is burnt together with part of bagasse and straw in the cogeneration system. An iterative process takes place to determine the fraction of bagasse and straw burnt to meet process steam requirements and the remaining amount is diverted for 2G process, which, consequently, alters steam demand. The convergence is only achieved when the energy (as steam) required by the process is equal to the energy produced in the cogeneration system.

In the 2G process, stoichiometric model reactors were used to represent pretreatment and hydrolysis reactors as well as the C5 fermentation (when considered). Solid-liquid separation units were modeled by component separators. As different technological scenarios were considered along this work, considered conversions and efficiencies are presented in the following chapters. An example of 2G process flowsheet is shown in Figure 13.

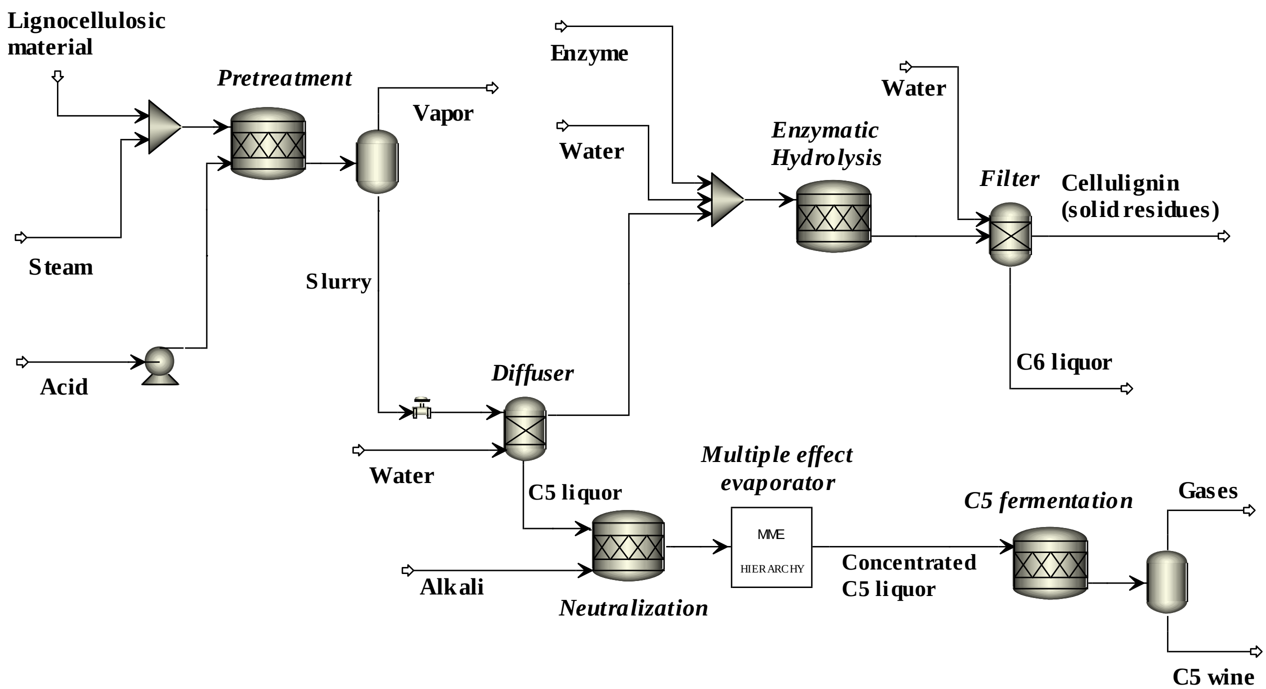

Figure 13. Process flowsheet of 2G process considering catalyzed steam explosion pretreatment and C5 fermentation.

3.2.3. Simulation of vinasse and C5 liquor biodigestion

The amount of vinasse ranges from 8 to 15 liters per liter of produced ethanol, depending on ethanol concentration in the wine and whether a reboiler (indirect heating) or a direct steam injection is used in the columns. Due to nutrients presence in vinasse, it can be spread in the fields for fertirrigation. Although not well-established in the sector, vinasse biodigestion (or anaerobic biodigestion) is a solution to reduce its organic content and produce biogas, which can be burnt to generate electricity or sold as natural gas replacement, among other alternatives.

For vinasse biodigestion, a simplified model based on a calculator block[9] and a HeatX model was considered. In the calculator block, the volume of biogas (Q_{biogas}), produced proportionally to vinasse flow ($Q_{vinasse}$), was calculated using the following equation:

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[9] Calculator block allows to incorporate Fortran statements or Microsoft Excel spreadsheets into the flowsheet calculations. This can be used to set input variables based on equations included by the user.

$$Q_{biogas} = \frac{Q_{vinasse} \times COD_{vinasse} \times \eta_{biod} \times \Omega_{CH4}}{f_{CH4}} \; [Nm^3/h] \qquad \text{(Equation 1)}$$

For an autonomous distillery, it was assumed that vinasse has a chemical oxygen demand (COD) of 21 kg/m³, from which 72 % can be removed through biodigestion (η_{biod}), producing methane at the proportion (Ω_{CH4}) of 0.29 Nm³/kg of COD removed. Biodigestion reactor is coupled to a treatment system for H_2S removal, resulting in a biogas composition (volumetric basis) of 60 % CH_4 (f_{CH4}) and 40 % CO_2, with a lower heating value (LHV) equal to 21.5 MJ/Nm³ (Moraes et al., 2014).

Potential energy obtained through combustion of biogas was estimated based on its LHV and boiler efficiency, which was considered equivalent to that using bagasse and straw. The calculated energy is used as input information in the heat exchanger placed after the boiler in the CHP unit, increasing hot gases temperature, and consequently, the amount of high pressure steam that can be produced.

Alternatively, the use of biogas as natural gas replacement was considered. In this scenario, CO_2 removal operation is considered to achieve CH_4 concentration up to 85 %.

When C5 liquor produced during pretreatment is biodigested, biogas was assumed to be used only as fuel, increasing the amount of surplus lignocellulosic material sent for 2G process. An approach similar to that described for vinasse biodigestion and biogas combustion was employed. However, COD in C5 liquor is very sensitive to the pretreatment used and no reference value was available in the literature. Therefore, COD was calculated based on potential oxidation of organic compounds present in C5 liquor (xylose, glucose, C5 and C6 oligomers, acetic acid and sucrose). In a first approach, due to little information available, efficiency and proportion of methane produced per mass of COD removed were considered equal to those assumed for vinasse.

3.2.4. Simulation of alternatives for extending operation period

<u>Operation of CHP all year-round</u>

In order to allow operating CHP unit in the sugarcane off-season, a fraction of the lignocellulosic material (bagasse and straw) is stored. With the purpose of minimizing idle capacity, it was defined that the same amount of fuel would be burnt in the boiler in both periods (season and off-season). Since off-season period (130 days) is shorter than season (200 days), the amount stored per hour is lower than the amount burnt in the boilers.

During the sugarcane season, part of the generated steam is not consumed in the process, and then it is expanded/condensed in extraction-condensing turbines to generate additional electricity; in the off-season, since there is almost no need of steam, electricity generation is maximized and all steam produced is expanded/condensed. The consideration that 50 % of straw is recovered from the field, through baling system, and is used as fuel allows reaching this balance.

<u>Sugarcane juice concentration</u>

In order to produce ethanol in the sugarcane off-season, sugarcane juice can be stored in a concentrated form (known as high test molasses – HTM). However, inversion of sucrose must be carried out to prevent sugar crystallization and degradation during concentration step. Different methods can be employed for inversion of sucrose, using sulphuric acid, ion exchanging resins and invertase (enzyme found in the conventional yeast *Saccharomyces Cerevisiae*). Acid inversion present as disadvantage sugars degradation (around 3-5%) due to high temperature in the presence of sulphuric acid (CHEN; CHOU, 1993); while resins are susceptible to saturation due to the presence of ashes, being recommended only for food grade inverted syrup (COPERSUCAR, 1985). Both references indicate enzymatic inversion as a suitable method for HTM production, thus it was considered in this study. Inversion of sucrose is carried out adding yeast in the concentrated juice (around 53% soluble solids), then the inverted juice is finally concentrated up to 85 % soluble solids (CHEN; CHOU, 1993).

From sugarcane reception and cleaning to juice treatment, the process is kept the same as a conventional autonomous distillery. However, concentration is performed using a 5-stage multiple effect evaporator; part of the juice, with concentration around 18 % soluble solids, is sent to fermentation; whereas the remaining juice is destined to HTM production.

The proportion of the juice that is concentrated and inverted for off-season operation (130 days) is defined in such a way that the feed of fermentation is the same all year-round (330 days).

Bagasse and straw are also stored to supply steam and electricity in the off-season. It was defined that the same amount of lignocellulosic material would be burnt in the boiler in both periods (season and off-season).

Use of sweet sorghum as drop-in feedstock

Sweet sorghum processing in the same facility as sugarcane (autonomous distillery) was considered for operation during sugarcane off-season.

Composition of sweet sorghum is presented in Table 7. Fibers composition was assumed to be the same as that of sugarcane.

Table 7. Composition of sweet sorghum - variety BRS511 (PARRELLA; SCHAFFERT, 2012).

Parameter	**Value**
Fibers (%)	11.1
Soluble solids (°Brix)	14.4
Pol (% sucrose)	10.6
% Reducing sugars (RS)[a]	1.0
Water content (%)	74.5

[a] Higher proportion between sucrose and reducing sugars in sweet sorghum composition are found in the literature (PACHECO, 2012), but there is no significant difference for simulation purposes, since all sucrose is converted into reducing sugars.

Sweet sorghum milling capacity was fixed equal to that of sugarcane (approximately 417 t/h). Two operation periods were defined:

- 28 days: based on the amount of sweet sorghum from sugarcane replanting areas (around 20 % of the area);

- 60 days: assuming that sweet sorghum can be purchased from independent producers to operate 60 days in the off-season.

A longer period can be considered, but it depends on climate conditions of each region as well as feedstock availability in the areas close to the mill.

Ethanol production from sweet sorghum is comprised by the same process steps of a sugarcane autonomous distillery, but different efficiencies were considered (see comparison on Table 8).

Table 8. Process efficiencies for ethanol production from sugarcane and sweet sorghum.

Parameters	**Sugarcane**	**Sweet sorghum**
Efficiency of sugars extraction	96 %	90 % [a]
Sucrose content in the filter cake [b]	1 %	3 % [a]
Fermentation efficiency	90 %	88 % [c]
Distillation efficiency	99 %	99 % [c]

[a] Values based on PACHECO (2012);

[b] Represents losses on juice treatment;

[c] It was assumed that fermentation efficiency would be lower for sweet sorghum processing due to possible presence of inhibitors, but distillation efficiency would not be affected.

It was also considered that sweet sorghum bagasse can be used as fuel in the CHP to supply steam and electricity, maintaining the boiler and turbines efficiencies. Therefore, it was assumed that all sugarcane bagasse and straw are burnt during the season.

Second generation process

Unlike the previous alternatives, it was assumed that 2G process runs all year-round (330 days). If 2G process did not take place also during the season, the additional processing section – including pretreatment, hydrolysis and C5 fermentation – would be idle in this period. Although C6 was fermented without juice addition, no reduction on yields was assumed for off-season.

In order to simulate this alternative, bagasse and straw are divided in three streams, the first one is sent to CHP unit along with residual cellulignin to supply energy to the process; the second stream is destined for 2G ethanol production; the third one is stored to operate 2G process in the off-season. The iterative process becomes more complex, since the third parcel must be enough to supply the energy (complementing residual solids combustion) and operate 2G process at full capacity during 130 days.

An auxiliary simulation was created to represent operation in the off-season period. Although the capacity of 2G process was kept the same all year-round, the process areas shared with 1G process operate with lower flows in the off-season. The same applies for CHP unit, since steam consumption is much lower in the off-season compared to season, when 1G process is also operational.

As most facilities maintain multiple pieces of equipment for the same function, it is not expected a decrease on efficiencies due to operation outside of the specified flow. In practice, some equipment will be idle in the off-season period.

3.3. Investment estimation and economic analysis

3.3.1. Investment estimation

Investment estimation was based on VSB's internal databank and methodology. Techno-economic assessment was carried out considering greenfield projects, i.e. new facilities, thus overall investment was taken into account instead of incremental investment. It is worthwhile to mention that this approach provides a good indicative on biorefineries feasibility, without the need to detail an existent plant.

For 1G process, reliable data for investment is available, since it is a well-know and consolidated process. The approach consisted on calculating the investment cost per area considering the distribution presented on Table 9. The values refer to a basic configuration (not optimized in terms of energy) for a plant processing 2 million tonnes of sugarcane per year, employing low pressure boilers, azeotropic distillation as dehydration method and direct drivers and, consequently, presenting a high steam consumption and no electricity surplus.

Table 9. Investment for basic scenarios in 2009 values (CTBE, 2012).

Item	Investment (million R$)[a]	
	Basic annexed distillery	Basic autonomous distillery
Steam generation system [b]	51	36
Reception /Extraction system	41	45
Distillery	31	54
Sugar factory	31	0
Turbines/electricity generators	20	18
Other equipment	31	27
Electromechanical assembly	24	21
Civil works	44	39
Electrical installations	27	24
Instrumentation/Automation	7	6
Engineering services, thermal insulation and painting	34	30
Total	**340**	**300**

[a] Average exchange rate US$ 1.00=R$ 2.29 from January to July of 2014.

[b] Steam demand around 550 and 500 kg/TC was considered for annexed and autonomous distilleries, respectively.

A cost-capacity equation with 0.6 exponent was employed to estimate cost for different capacities, for instance, in the scenarios with extended period of operation, since lower hourly processing capacities are expected. In this approach, the main flows obtained from process simulation are used as inputs for the cost-capacity equation, such as sugarcane processing, steam and ethanol production. As an example, the steam production is used to estimate investment on cogeneration system.

In order to differentiate basic and optimized configurations, some assumptions were considered:

- Increase of 30 % in the sections “Steam generation system” and “Turbines/electricity generators” when 65 bar boilers are used (CTBE, 2012);
- Increase of 40 % in the item “Distillery” when, instead of azeotropic distillation, molecular sieves are used to produce anhydrous ethanol (CTBE, 2012);

- Increase of 10% on “Distillery” and “Sugar factory” when thermal integration was assumed for inclusion of a exchanger network (CTBE, 2012);
- Additional investment on transmission lines of R$ 19.2 million in 2009 value (CTBE, 2012).

These estimations were updated to Jul/2014 using IPCA (Extended National Consumer Price Index).

For alternative process configurations, additional and more detailed information were required, e.g., estimations for storage tanks, multiple effect evaporators and biodigestion system and biogas purification. Some reference values retrieved from VSB`s databank are presented in Table 10:

Table 10. Investment on additional equipment (2014 values).

Item	Reference flow	Investment (million R$)
Storage tanks	HTM: 5000 m³	1.6
Multiple effect evaporator	Evaporated water: 180 m³/h	19.5
Biodigestion system	COD[a] load: 175 t/d	19.8
CO_2 removal from biogas	Biogas: 145 t/d	0.1

[a] COD – chemical oxygen demand.

Regarding 2G process, more uncertainties on investment estimation are expected as it is an incipient technology and process configuration is still not consolidated. In this case, the methodology was based on estimation of the main equipment (e.g., pretreatment and hydrolysis reactors) and a factor to represent auxiliary equipment was defined for each area. Reference values for each area are presented in Table 11. Besides, it was considered that the equipment cost is a fraction (35 %) of the overall 2G investment (installed cost).

Since most 2G equipment estimations were located in U.S., CEPCI (Chemical Engineering Plant Cost Index) to update values to Jul/2014 and exchange rate US$ 1.00=R$ 2.29 were considered.

Table 11. Investment for each area of 2G process (2014 values).

Area	Reference flow	Investment (million R$)[a]
Pretreatment (residence time: 10 min)	Insoluble solids: 20 t/h	14.3
C5 separation (diffuser)	Insoluble solids: 10 t/h	13.6
Hydrolysis	Insoluble solids: 15 t/h Total flow: 100 t/h	12.5 [b]
C6 separation (Oliver filter)	Insoluble solids: 10 t/h	10.0

[a] Investment figures are not directly comparable, since they are related to specific flows. No location factor for Brazil was assumed.

[b] Reference values represent equipment for 12 h of liquefaction (high viscosity material) and 36 h of hydrolysis, totalizing 48h residence time.

3.3.2. Economic analysis

Traditional economic impacts, based on Economic Engineering, were calculated, such as internal rate of return, net present value and ethanol production cost in order to allow comparison between the evaluated scenarios.

Market prices for feedstock, inputs and products were used to calculate expenses and revenues. These values, along with investment cost, are employed to build the cash flow. Project lifetime of 25 years is assumed, requiring 2 years for construction and start-up of the plant. Linear depreciation was assumed as well, considering a 10-year period of time and that there is no salvage value of equipment at the end of the lifetime period. Tax rate (income and social contributions) was assumed as 34 %.

Internal rate of return (IRR) is the interest rate that balances all operating profits along the project life time and the investment. The higher the internal rate of return, the more attractive is the project. The following mathematical expression was used to calculate the IRR, considering a life time of 25 years (CTBE, 2012):

$$\sum_{k=1}^{25} \frac{Operating\ profit\ (k)}{(1+IRR)^k} = Total\ investment \qquad \text{(Equation 2)}$$

The net present value (NPV) is defined as the sum of the present values of incoming and outgoing cash flows over a period of time. All cash flows need to be adjusted to the same time reference using a discount rate. The discount rate, or in this case, the minimum attractive rate of return (MARR) is defined based on the expected return of other investment choices with a similar level of risk (CORREIA NETO, 2009). If the NPV results in zero, the IRR is equal to the MARR. For a positive NPV, the project is economically attractive.

With the purpose of calculating the ethanol production cost, the expenses were allocated among all the products proportionally to their participation on revenues, resulting in the operational expenditure (OPEX). In order to calculate the capital expenditure (CAPEX), the capital was considered to be remunerated using a discount rate of 12 %. Alternatively, the production costs of the biorefinery products were calculated reducing proportionally their market prices until the IRR equals to zero. In other words, all the expenses (including capital depreciation) are allocated proportionally to the revenue of each product.

4. Sugarcane biorefineries

The following manuscript **"Sugarcane biorefinery: product diversification impacts on first generation ethanol feasibility"**, evaluates the integration of efficient cogeneration systems – considering high pressure boilers (65 bar) and extraction-condensing turbines – using straw, sugar production unit and vinasse biodigestion process in a 1G ethanol production facility. The main objective is to assess the impacts of product diversification in the techno-economic feasibility of a sugarcane biorefinery. Besides, the flexibility to produce more ethanol or sugar according to the market trends was also evaluated.

Sugarcane biorefinery: product diversification impacts on first generation ethanol feasibility

Abstract

In Brazil, conventional ethanol production is based on sugarcane juice fermentation, which is considered a first generation production process. This process takes place in annexed plants and autonomous distilleries; the latter produces ethanol and the former also has sugar as product. Both types of plants produce steam and electricity from sugarcane bagasse to supply the process and, in some cases, to sell electricity surplus to the grid. Additional electricity can be generated using sugarcane straw as complementary fuel besides an efficient cogeneration system. Sugarcane biorefineries also produce large volumes of vinasse that is an effluent from ethanol distillation process, commonly spread in the field (fertirrigation) without any previous treatment. In this work, efficient cogeneration systems using straw, sugar production unit and vinasse biodigestion process were integrated to the ethanol production process in order to assess the impacts of co-products generation on the feasibility of first generation ethanol production plants. Results showed that energy optimization, use of straw and production of other products (electricity, sugar and biogas), in addition to ethanol, improved techno-economic feasibility, reducing ethanol production cost (up to 10 %) and increasing net present value (NPV) and internal rate of return (IRR) of the plant. Besides, diversification of products diminishes

susceptibility to market oscillations, improving business stability. Flexibility also proved to be a key point for annexed plants, which allows producing more sugar or ethanol according to market demands, maximizing revenues.

Keywords: Sugarcane biorefinery, first generation ethanol, sugar, biodigestion, techno-economic analysis.

Introduction

The biorefinery concept embraces a wide range of technologies able to separate biomass resources (wood, grasses, corn, etc) into their building blocks (e.g. carbohydrates) which can be converted to value-added products, biofuels and chemicals. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce biofuels for mobility, power, and chemicals from biomass. This concept is analogous to a petroleum refinery, which produces multiple fuels and products from petroleum (Cherubini, 2010).

Brazilian sugarcane mills fit into the biorefinery concept, since ethanol, sugar and electricity can be produced from sugarcane. Sugarcane products (ethanol and electricity) represent almost 18 % of primary energy production and 38 % of renewable energy produced in Brazil (EPE, 2013). In 2014/2015 season, the prospect was for a 660 million tonnes of sugarcane harvest, in a cropland area of approximately 9 million hectares, being 53.9 % of total sugarcane (based on sugar equivalence) destined for ethanol production (CONAB, 2014).

The first generation ethanol production (from sugarcane juice) is a well-established process, since Brazil has been producing fuel ethanol through fermentation of the sugarcane juice on a large scale basis for more than 30 years (Costa and Sodré, 2010). Ethanol production from sugarcane takes place in autonomous distilleries or annexed plants; in the latter a fraction of the sugarcane juice is diverted for sugar production and the remaining fraction along with the molasses (solution of sugars that remains after sucrose crystallization) are used for ethanol production. In 2011/2012 season, approximately 64 % of the sugarcane processing units in Brazil were annexed plants (CONAB, 2013). The flexibility of annexed plants to produce variable amounts of ethanol and sugar, depending upon the market demands and climate conditions, is part of the reason for the success of bioethanol production in the country (Cavalett et al., 2012).

In both types of facilities, steam and electricity are produced to supply process demand in the cogeneration system (combined heat and power generation) using bagasse, and sometimes straw (sugarcane tops and leaves), as fuel. These plants are self-sufficient in energy and, when connected to the grid, can sell electricity surplus (amount that exceeds the plant requirements). The valorization of electricity since the end of the last decade and the prospect of selling to public utility concessionaires have stimulated a new cycle of modernization of cogeneration systems with plants installing high pressure systems (e.g., 65 bar) that permit to increase electricity surplus (BNDES and CGEE, 2008). Crago et al. (2010) pointed out that the credit from sales of electricity would increase ethanol competitiveness when compared to U.S. corn ethanol, reducing sugarcane ethanol production cost.

Another relevant output of sugarcane mills is vinasse (also called stillage), which is an aqueous residue from ethanol distillation process, produced in a proportion of approximately 13 L of vinasse for each liter of alcohol (Salomon and Lora, 2009). Vinasse has a high polluting potential if wrongly handled and, although it is not considered a product, its large volume justifies a special attention regarding treatment and disposal. The most common destination of this effluent is on soil as fertilizer – namely fertirrigation – for sugarcane cultivation because of its content of organic matter and nutrients (mainly potassium but also nitrogen and phosphorus). From an economic perspective, this application represents the least expensive and simplest solution for discharging this voluminous effluent based on Brazilian environmental legislation; however, there are uncertainties on environmental impacts even though it is allowed by law (Moraes et al., 2014). Additional concern related to vinasse generation is expected due to implementation of second generation process (ethanol production from lignocellulosic materials), increasing the amount generated and organic matter content.

In this context, anaerobic digestion prior to fertirrigation has been considered an effective method for reducing COD (chemical oxygen demand) of vinasse and converting it to biogas, which is a readily usable fuel for the ethanol facility. Nutrients in the vinasse – macro-nutrients (N, P, and K), micro-nutrients (Fe, Zn, Mn, Cu, and Mg), and nonessential metals – are generally conserved through anaerobic digestion, while the majority of the organic content is removed (Wilkie et al., 2000).

In Brazil, nowadays, there are 25 biogas plants connected to the electricity grid, most of them located on agricultural properties to process residues and on landfills (IEA, 2013). Another Brazilian application example is the small scale family farms in the State of Paraná, which inject raw biogas into a 22 km-long pipeline to a central position to produce electricity and heat or to be upgraded to biomethane and used locally as a vehicle fuel (Thrän et al., 2014).

In this work, techno-economic assessment of biorefinery alternatives is presented, showing the impacts of co-products generation on the feasibility of first generation ethanol production plants. For this purpose, efficient cogeneration system, sugar production unit and vinasse anaerobic digestion process (here referred as biodigestion) were integrated in an autonomous distillery using the Virtual Sugarcane Biorefinery (VSB). VSB is a comprehensive framework – developed by Brazilian Bioethanol Science and Technology Laboratory (CTBE) – that integrates computer simulation platforms with economic, social, and environmental evaluation tools to allow comparison of alternative technologies and/or development stages as well as process optimization (Cavalett et al., 2012).

In addition, this work intends to provide an overview of technology alternatives that already exist in sugarcane mills (to a greater or lesser extent) and are available in the sector to retrofit an existing facility or as part of a new installation. Assessment of these alternatives – using the same methodology, process parameters, economic assumptions and prices – establishes a basis for comparison and, consequently, support decision making process.

Methods

Process Simulation

Optimization features

Several studies in literature evaluated alternatives to reduce steam consumption in the ethanol production process (Ensinas et al., 2007; Dias et al., 2011). In the present work, thermal integration and molecular sieves for dehydration process were considered for reduction on steam demand. Aiming at increasing energy efficiency, steam turbines as mechanical drivers were replaced by electrical engines and high pressure boilers (65 bar) were considered instead of 22 bar boilers. Basic configuration represents an average plant of Brazilian sugar-energy sector, while the optimized configuration represents plants installed in the last few years. A summary of basic and optimization features is presented in Table 1.

Table 1. Configuration of autonomous distilleries (basic and optimized scenarios).

Characteristic	**Basic Distillery**	**Optimized Distillery**
Energy demand	Mechanical: 16 kWh/TC* (mechanical drivers) Electric: 12 kWh/TC*	Electric: 30 kWh/TC* (electrical drivers)
Reduction on steam demand (2.5 bar steam)	0 %	20 %
Dehydration process	Azeotropic distillation (2.0 kg steam/L ethanol)	Molecular sieves (0.6 kg steam/L ethanol)
Bagasse destination	No surplus bagasse	Surplus bagasse is burnt
Boiler pressure	22 bar (75 % efficiency)	65 bar (87.7 % efficiency)
Type of turbine	Back-pressure (72 % efficiency)	Extraction – Condensing (85 % efficiency)

* Specific values per tonne of cane (TC).

Optimization focused on reduction of overall energy consumption and increase of electricity generation. Towards this objective, the use of straw as fuel in the boilers presents a great opportunity, since it accounts for 1/3 of the energy potential of sugarcane (Pippo et al., 2011). In the last few years, transition from manual to mechanized harvesting, which was encouraged by the prohibition of burning previous to harvest, led to an increase on straw availability in the field. Cardoso et al. (2013) compared two alternative methods of straw recovery – integral harvesting and baling systems – and estimated cost considering different recovery fractions (from 30 to 70 %). The amount of straw that must be left on the field depends on specific conditions of the sugarcane field, such as location, cane variety, stage of cut, harvesting period, climate and other combined aspects (Hassuani et al., 2005).

Straw is produced in a proportion of 140 kg (dry basis) per tonne of sugarcane (wet basis). In the case that straw is used as fuel in the boilers, it was assumed that 50 % of straw (with 15 % moisture) would be recovered from the field through baling system. Same cogeneration efficiency was considered for both bagasse and straw.

Three scenarios were considered in order to evaluate impacts of electricity production in an autonomous distillery:

- Basic autonomous distillery (S1) – steam consumption around 520 kg steam/TC;
- Optimized autonomous distillery (S2) – steam consumption around 340 kg steam/TC;
- Optimized autonomous distillery with straw recovery (S3) – idem S2;

Vinasse Biodigestion

Vinasse biodigestion prior to application in the field was considered. Two scenarios were defined based on the alternative uses of biogas:

- Optimized autonomous distillery with straw recovery, biodigestion of vinasse and use of biogas for electricity production (S4)
- Optimized autonomous distillery with straw recovery, biodigestion of vinasse and selling of upgraded biogas considering a price equivalent to natural gas, based on low heating value (S5)

Data for biodigestion of vinasse was based on Moraes et al. (2014). It was assumed that the vinasse from an autonomous distillery has a chemical oxygen demand (COD) of 21 kg/m³, from which 72 % can be removed through biodigestion (η_{biod}), producing methane at the proportion (Ω_{CH4}) of 0.29 Nm³/kg of COD removed.

A simplified model, described by Equation 1, was used to estimate biogas production (Q_{biogas}) based on the vinasse flow ($Q_{vinasse}$) and the previous assumptions. It was assumed that biodigestion reactor is coupled to a treatment system for H_2S removal from biogas, resulting in a composition (volumetric basis) of 60 % CH_4 (f_{CH4}) and 40 % CO_2.

$$Q_{biogas} = \frac{Q_{vinasse} \times COD_{vinasse} \times \eta_{biod} \times \Omega_{CH4}}{f_{CH4}} \; [Nm^3/h] \quad (1)$$

For scenario 4, potential energy obtained through combustion of biogas was estimated based on its lower heating value (LHV) equal to 21.5 MJ/Nm³ (60 % CH_4). Biogas is burnt in the combined heat and power generation system (CHP) with the same boiler efficiency considered for bagasse and straw. In the simulation, the value calculated using Equation 1 is added to the energy obtained in the boiler from bagasse and straw combustion, increasing the generated amount of high pressure steam.

In scenario 5, biogas undergoes an operation of CO_2 removal, increasing CH_4 concentration up to 85 % (upgraded biogas or biomethane). Since biogas production oscillates and the demand is usually stable, gas holders are used for storage. The most common gas holder is the low pressure type that maintains overpressure between 0.5 and 30 mbar, while higher pressure gas holders (5 to 250 bar) are expensive and have high operational cost (FNR, 2010).

Flexibility of annexed plants

Integration of sugar production was evaluated, considering two scenarios:

- Optimized annexed plant 50:50 with straw recovery (S6) – sugarcane juice is diverted at the same proportion to produce ethanol and sugar.

- Optimized annexed plant with straw recovery and flexible configuration 70:70 (S7) – 30 to 70 % of sugarcane juice can be sent to each product, depending on market trends, aiming at maximizing revenues.

The flexible configuration was simulated considering two situations: when there is high price for ethanol, the flexible plant would operate equal to an annexed plant 70:30 (ethanol: sugar); if sugar market is favorable, it would work as an annexed plant 30:70.

General assumptions

The capacity of the evaluated biorefineries was assumed equal to 2 million tonnes of sugarcane per year, operating 200 days per year.

The ethanol production process consists of sugarcane cleaning and extraction, juice treatment and evaporation, fermentation, distillation and dehydration. In the case of an annexed plant, part of the sugarcane juice is further concentrated and then sent to crystallization and drying to produce sugar. Molasses, a concentrated residual solution generated during sugar production, is also fermented to ethanol (Cavalett et al., 2012). Bagasse, generated during juice extraction, is used as fuel in the cogeneration system to produce steam and electricity. If straw is recovered, even partially, from the field, it can be used as a complementary fuel in the boilers.

Process simulation was carried out using Aspen Plus®, considering operating conditions and efficiencies based on Brazilian sugarcane industry: 96 % sugar extraction efficiency, 90 and 89.5 % for fermentation yield for autonomous and annexed plant, respectively, and 76.5 % recovery of sugars in the final sugar. Detailed operating and process parameters are described in CTBE (2012).

Figure 1 illustrates the main process steps considered for evaluation of the alternatives and Table 2 summarizes the characteristics of the proposed scenarios.

Table 2. Description of proposed scenarios.

Characteristic	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Autonomous distillery	X	X	X	X	X		
Annexed plant						X	X [a]
Basic configuration	X						
Optimized configuration		X	X	X	X	X	X
Use of straw			X	X	X	X	X
Biogas production				X [b]	X [c]		

[a] flexible plant;

[b] biogas used as fuel;

[c] biogas as substitute of natural gas.

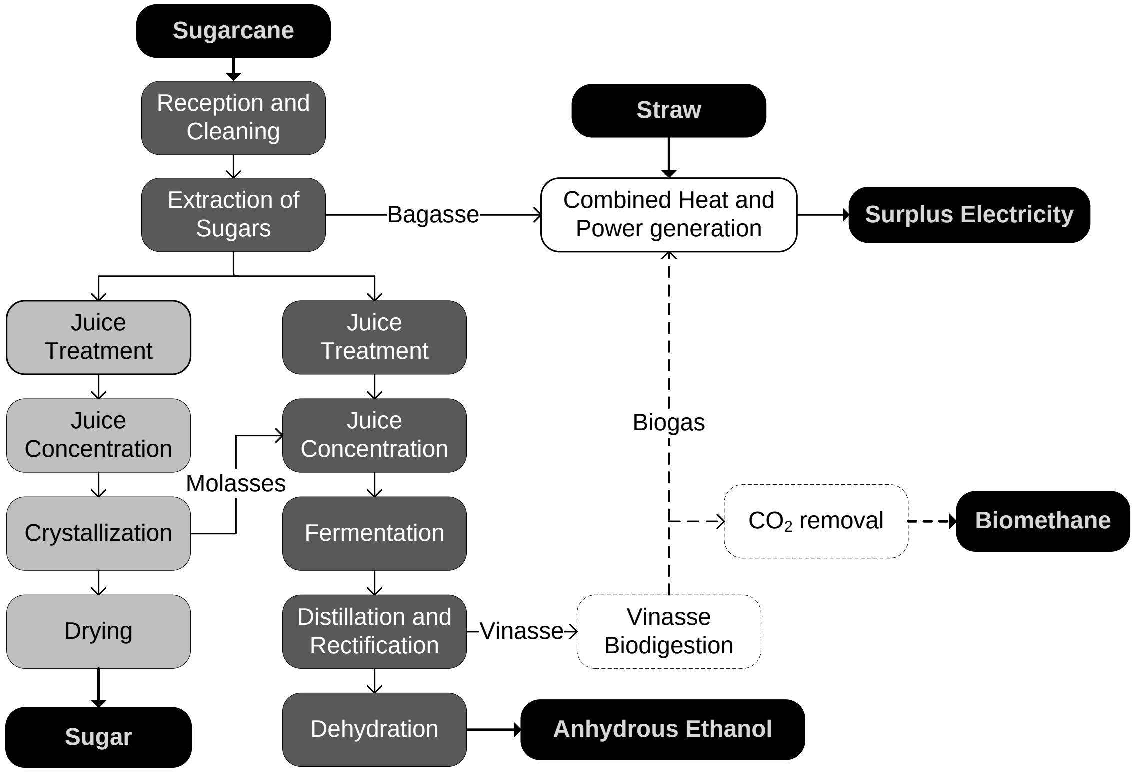

Figure 1. Block flow diagram considering all the studied biorefinery alternatives. Black blocks represent feedstock and products; dark grey blocks, ethanol production process; light grey blocks are additional unit operations required for sugar production; dashed lines represent vinasse biodigestion alternatives.

Economic Evaluation

A cash flow analysis was performed, considering feedstock costs and products prices (Table 3) as well as the results of process simulation to calculate annual operational costs and revenues.

Information about prices were gathered for the last ten years, when available, updated to Jul/2014 values using inflation rate, then a 6-year moving average was calculated for the prices available in monthly basis. Fixed capital investment was estimated based on The Virtual Sugarcane Biorefinery (VSB) - 2011 Report (CTBE, 2012) and on estimates from specialists and engineering companies. The approach considered the main processing areas and investment for each one was estimated as a function of the main flows (e.g. processed sugarcane, production of ethanol and steam) using a cost capacity exponent equal to 0.6. Besides the conventional steps included in the sugarcane mills, investment on biodigestion and biogas purification equipment was estimated.

Table 3. Prices considered in this assessment (exchange rate US$ 1.00=R$ 2.29).

Product	Specification	Historical Average	Observations
Sugarcane (US$/t)	13 % fibers 15.3 % sugars 70 % moisture	24.04	Prices for São Paulo State (UDOP, 2014), from Aug/2005 to Jul/2014
Sugarcane straw (US$/t)	15 % moisture	29.55	Estimated based on 50 % straw recovery through baling system (Cardoso et al., 2013)
Anhydrous ethanol (US$/L)	99.6 % ethanol	0.59	Prices for São Paulo State (CEPEA, 2014), from Aug/2005 to Jul/2014
Sugar (US$/kg)	99.6 % purity 0.1 % moisture	0.44	Prices for São Paulo State (CEPEA, 2014), considering an average of VHP and crystal sugar prices from Aug/2005 to Jul/2014
Electricity (US$/MWh)	-	57.83	Prices for electricity from sugarcane bagasse in national auctions (MME, 2014), from 2005 to 2013
Biomethane (US$/m³)	85 % methane	0.60	Based on natural gas prices, considering energy equivalency, for São Paulo State from 2004 to 2013 (ANP, 2014)

Economic impacts were assessed taking into account internal rate of return, net present value and ethanol production cost. Project lifetime of 25 years is assumed as well as 2 years for construction and start-up of the plant. Linear depreciation was assumed, considering a 10-year period of time and no salvage value of equipment at the end of the lifetime period. Tax rate (income and social contributions) was assumed as 34 %. The annual capital cost was calculated as the payment of the investment at the minimum acceptable rate of return (12 % per annum) considering a 25-year period.

In order to compare both annexed plant scenarios (S6 and S7) and simulate the flexibility, monthly prices (updated to Jul/2014) for feedstock and products for a 10-year period (2005 -

2014) were considered. It was assumed that this cycle would be repeated for the entire plant lifetime (25 years). Ten years cycle of sugar and anhydrous ethanol price is presented in Figure 2. Cash flow was designed considering monthly operational costs and revenues.

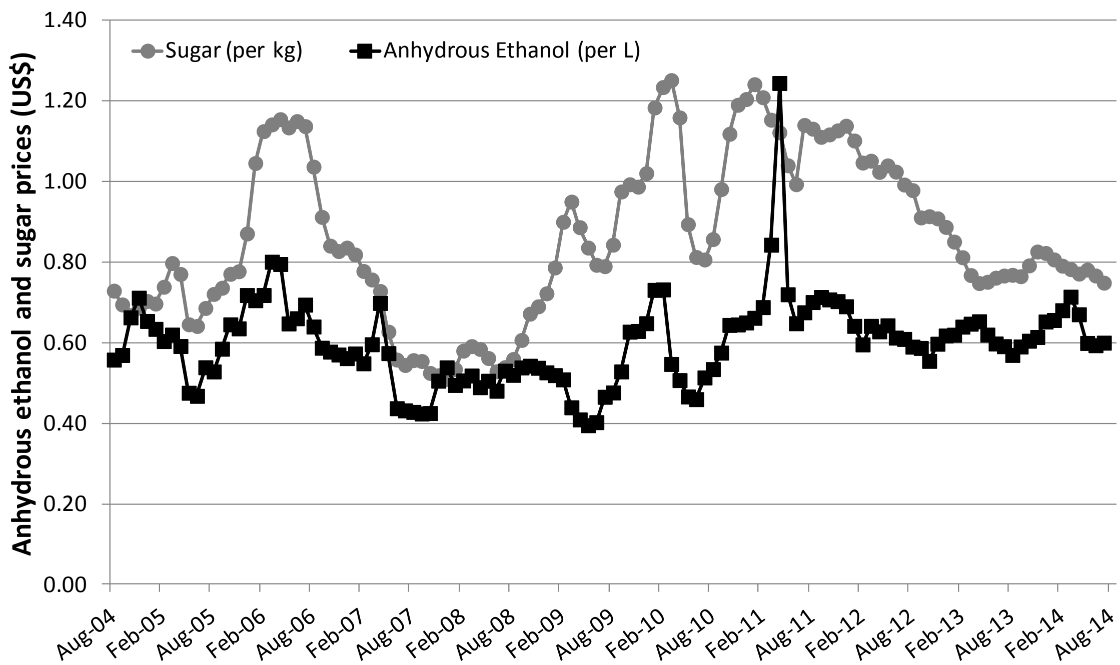

Figure 2. Prices for sugar (average of VHP and crystal) and anhydrous ethanol, in São Paulo State from Aug/2004 to Jul/2014 (CEPEA, 2014), values updated to Jul/2014.

From Figure 2, large and periodic oscillations are observed for both products. Market prices for ethanol and sugar in Brazil are impacted by many factors, especially seasonality of the feedstock, gasoline prices and international and domestic demand for sugar.

Results and discussion

Production of ethanol, sugar, electricity and biogas, estimated through process simulation for each scenario, is presented in Table 4.

Table 4. Biorefinery products in each scenario.

Product	S1	S2	S3	S4	S5	S6	S7*
Anhydrous ethanol (L/TC)	84.8	84.9	84.9	84.9	84.9	53.4	41.0-65.8
Sugar (kg/TC)	-	-	-	-	-	51.1	71.6-30.7
Electricity (kWh/TC)	-	91.6	195.1	206.2	195.1	194.0	192.5-193.7
Biomethane (m^3/TC)	-	-	-	-	4.3	-	-

* First value obtained when 70 % of sugarcane is diverted to ethanol, second one refers to 30 %.

Ethanol production in the scenarios based on autonomous distilleries (S1-S5) did not vary. Although only half of juice is fermented in the annexed plant (S6), due to molasses processing, ethanol production is about 60 % of that produced in the autonomous distilleries.

Basic distillery did not produce enough electricity surplus to justify investments on transmission lines to be connected to the grid and sell electricity; for this reason, electricity was not considered as product in scenario 1. Surplus electricity was 91.6 kWh/TC when all bagasse was burnt in an optimized plant (S2), and practically doubled with introduction of straw as complementary fuel. The inclusion of vinasse biodigestion – scenarios S4 and S5 – resulted in a small increase of electricity surplus (about 11 kWh/TC) and around 4 m^3/TC of biomethane, respectively. The annexed plant scenarios (S6 and S7) presented similar electricity surplus to the equivalent autonomous plant (S3), since optimization and straw use were considered as well.

Investment was calculated for each scenario (Figure 3) taking into account the main process streams: processed sugarcane and production of ethanol, sugar, steam and biogas. Heat exchanger network and transmission lines were calculated only for optimized scenarios, since basic configuration does not have thermal integration or electricity surplus. Flexible plant (S7) has the highest investment since sugar factory and distillery were sized based on maximum production of both products (processing 70 % sugarcane juice), which means that part of the plant capacity is always idle. In scenarios S4 and S5, a 5% increase on the biorefinery investment was observed due to the inclusion of biodigestion (compared to S3).

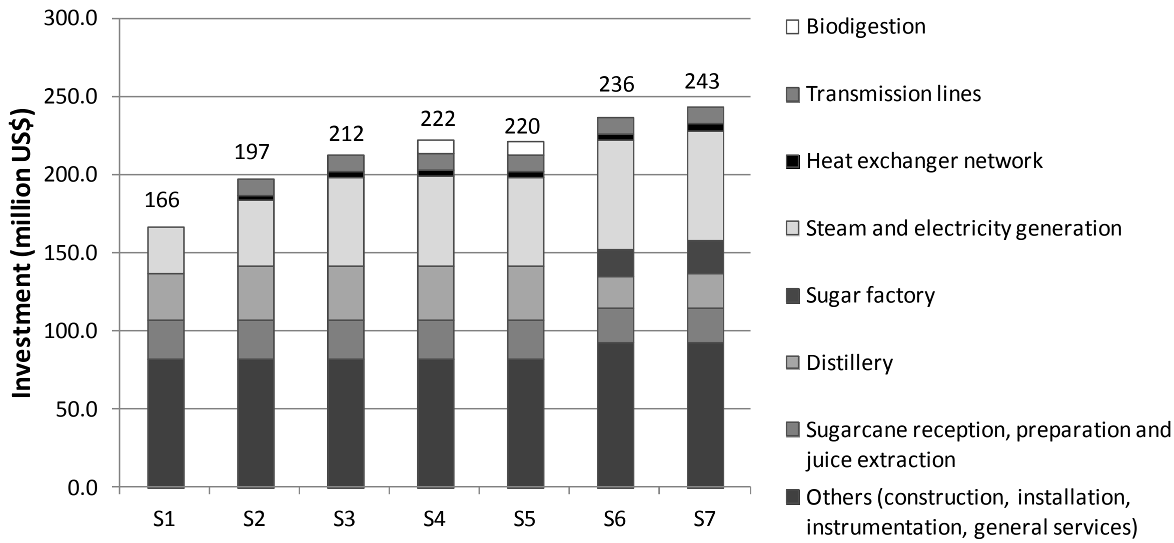

Figure 3. Distribution of investment per area of the plant and capital fixed investment for each scenario.

Figure 4 depicts participation of each product on revenues according to their production and selling prices.

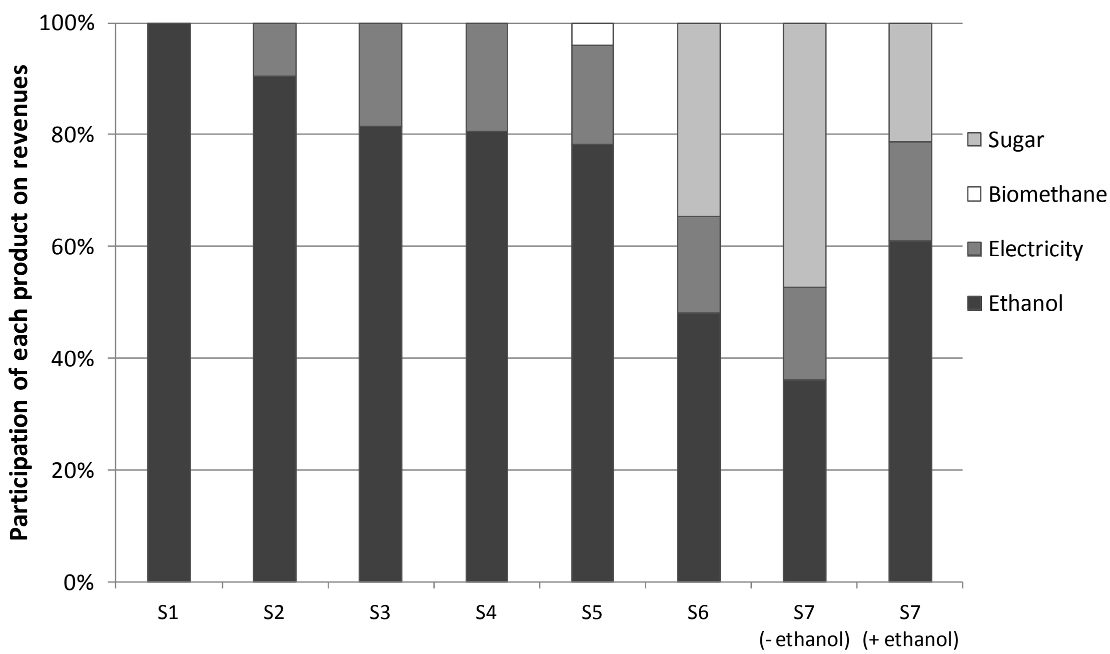

Figure 4. Participation of products on revenues for each scenario.

From Figure 4, it can be observed that ethanol participation on revenues decreased along the scenarios due to products diversification (electricity, biogas and sugar) and, consequently, ethanol production cost reduced due to allocation of operation (OPEX) and capital costs (CAPEX), as can be seen in Figure 5. Ethanol production cost varied between US$ 0.47/L (S6) and US$ 0.53/L (S1), which corresponds to a 10 % difference.

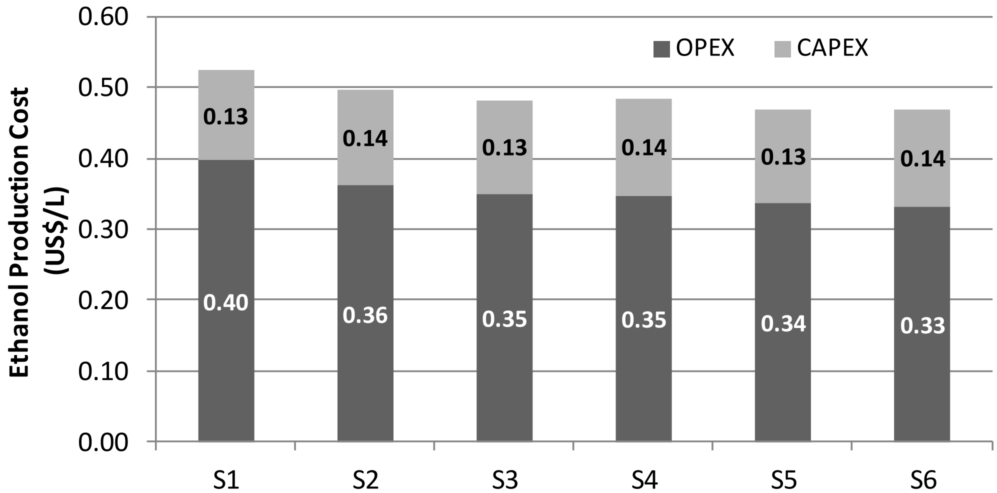

Figure 5. Contribution of OPEX and CAPEX in the ethanol production cost.

A comparison of the scenarios was carried out using internal rate of return (IRR) and net present value (NPV) as economic indicators (Figure 6). Flexible scenario (S7) was not included, because, unlike others scenarios, it considered a monthly-based analysis and is dependent on market considerations.

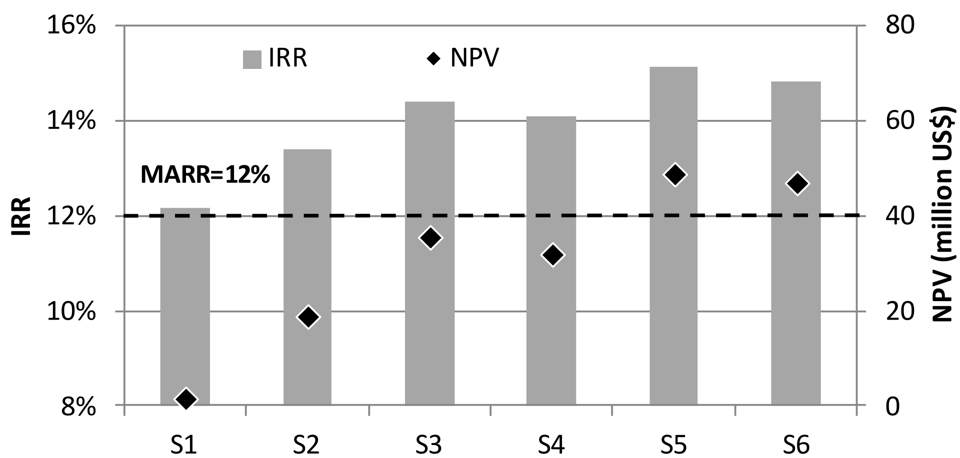

Figure 6. Internal rate of return and net present value for the evaluated scenarios.

Basic distillery (S1) achieved an IRR very close to the minimum acceptable rate of return (MARR) defined in this work (12 %); for this reason, NPV was almost zero for this case. Increase of electricity generation allowed an IRR of 13.4 % and 14.4 % for scenarios 2 and 3. The inclusion of biodigestion to produce more electricity (S4) did not pay off, since its IRR and NPV were lower than those of S3. However, if biomethane can be sold with an equivalent price to natural gas (in terms of energy), IRR would be 15.1 % and US$ 49 million of NPV would be achieved, being the most attractive alternative among evaluated scenarios.

It is worthwhile to mention that, different from the other scenarios assessed, the inclusion of biodigestion (S4 and S5) is not consolidated in the sector and these results were obtained based on a preliminary evaluation. Besides, further information on biomethane production and commercialization, such as product specifications, storage and distribution costs, must be taken into account before drawing definitive conclusions.

Comparing optimized autonomous distillery (S3) and annexed plant 50:50 (S6), the latter presented an increase on IRR and NPV, showing that sugar production can also be an interesting co-product.

Evaluation of monthly prices indicated that it was more profitable to produce sugar, since 76 % of the period the flexible plant operated maximizing sugar production. Internal rate of return of the flexible plant (15.4 %) was slightly higher than annexed plant 50:50 (15.0 %).

In order to demonstrate the potential of flexibility, Figure 7 presents a sensitivity analysis based on internal rate of return, considering increase on ethanol or sugar prices. The IRR of the flexible plant (S7) was higher than that of annexed plant 50:50 (S6) for all considered cases, but it was more sensitive to increase on sugar price, when benefits of flexible plant were enhanced.

Flexible annexed plants presents as advantage product diversification (including sugar, ethanol and electricity in their portfolio), which, combined with flexibility, decreases the effect of market oscillations on the revenues, ensuring business stability.

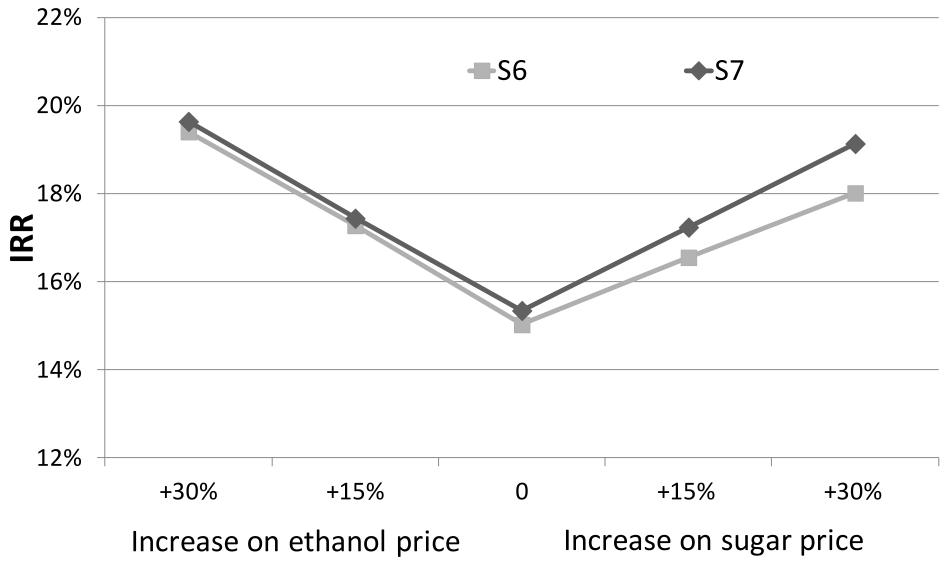

Figure 7. Sensitivity analysis for annexed plants.

Conclusions

This work provided an overview of technology alternatives that already exist in sugarcane mills (to a greater or lesser extent) and are available in the sector to retrofit an existing facility or as part of a new installation.

The possibility of selling electricity to the grid has motivated energy optimization of sugarcane biorefineries and investments on high pressure cogeneration systems. In addition, the use of straw as fuel in the boilers has potential to double electricity surplus.

Utilization of vinasse to produce biogas through anaerobic digestion was evaluated, showing that it is more economically attractive for the case biogas is sold as substitute of natural gas, while the use of biogas as fuel to produce electricity presented a slightly lower IRR compared to a scenario without biodigestion. However the biogas selling is conditioned to the existence of a connection to the grid. It is important to mention that other factors are relevant in the decision making to include vinasse biodigestion in the plant, such as reduce odor (avoiding insects), possible future changes in disposal regulation and the possibility to concentrate vinasse without increasing organic content, allowing application in longer distances.

Assessment of annexed plants showed that sugar production can improve ethanol feasibility and can also take advantage from flexibility, producing more sugar or ethanol depending upon the market demands. Although flexible plants require higher investment, increase on IRR was achieved and this difference was larger when increase on sugar or ethanol prices was considered.

Acknowledgment

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References

ANP - National Agency of Petroleum, Natural Gas and Biofuels (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis). 2014. Available from: http://www.anp.gov.br/. (in Portuguese). Accessed on August 2014.

BNDES and CGEE (Coord.). Sugarcane-based bioethanol – energy for sustainable development. Rio de Janeiro: BNDES, 2008.

Cardoso, T. F., Cavalett, O., Chagas, M. F., Morais, E. R., Carvalho, J. L. N., Franco, H. C. J., Galdos, M. V., Scarpare, F. V., Braunbeck, O. A., Cortez, L. A. B., Bonomi, A. Technical and economic assessment of trash recovery in the sugarcane bioenergy production system. Scientia Agricola, 70 (5), 353-360, 2013.

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. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. Clean Technol. Environ. Policy, 14: 399-410, 2012.

CEPEA - Center for Advanced Studies on Applied Economics (Centro de Estudos Avançados em Economia Aplicada). 2014. Available from: http://cepea.esalq.usp.br/english/. Accessed on August 2014.

Cherubini, F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management, 51, 1412–1421, 2010.

CONAB - National Supply Company (Companhia Nacional de Abastecimento). Monitoring of the Brazilian cane sugar harvest, v. 1 – season 2014/15 [Acompanhamento de safra brasileira Cana-de-açúcar, v. 1 – Safra 2014/15], n.2, Brasília, p. 1-20, 2014.

CONAB – National Supply Company (Companhia Nacional de Abastecimento), 2013. Profile of sugar and alcohol sectors in Brazil – season 2011/2012 [Perfil do Setor do Açúcar e do Álcool no Brasil - safra 2011/2012 (in portuguese). Brasília, v.5, p. 1-88, 2013.

Costa, R.C., Sodré, J.R. Hydrous ethanol vs. gasoline–ethanol blend: engine performance and emissions. Fuel, 89: 287–293, 2010.

Crago, C. L., Khanna, M., Barton, J., Giuliani, E., Amaral, W. Competitiveness of Brazilian sugarcane ethanol compared to US corn ethanol. Energy Policy, 38 (11), 7404–7415, 2010.

CTBE – Brazilian Bioethanol Science and Technology Laboratory. The Virtual Sugarcane Biorefinery (VSB): 2011 Report, 2012. Available online at: http://ctbe.cnpem.br/pesquisa/avaliacao-integrada-biorefinarias/. Accessed on January 2015.

Dias, M.O.S., Modesto, M., Ensinas, A.V., Nebra, S.A., Maciel Filho, R., Rossell, C.E.V.,. Improving bioethanol production from sugarcane: evaluation of distillation, thermal integration and cogeneration systems, Energy 36, 3691-3703, 2011.

Ensinas, A. V., Nebra, S.A., Lozano, M. A., Serra, L. M. Analysis of process steam demand reduction and electricity generation in sugar and ethanol production from sugarcane. Energy Conversion and Management, 48, 2978–2987, 2007.

EPE - Energy Research Company (Empresa de Pesquisa Energética). National Energy Balance 2013 – 2012 Base Year: Final Report, 2013. Available online at: http://www.mme.gov.br /mme/galerias/arquivos/publicacoes/BEN/2_-_BEN_-_Ano_ Base /1_-BEN_Portugues_-_Inglxs_-_Completo.pdf.

FNR - Fachagentur Nachwachsende Rohstoffe e.V.. Guia Prático do Biogás Geração e Utilização. 5th Ed. Gülzow, 2010.

Hassuani, S.J., Leal M.R.L.V., Macedo I.C. (eds). Biomass Power Generation—Sugarcane Bagasse and Trash. CTC and PNUD, Piracicaba, 2005.

IEA. Bio-Energy in family framing – a new sustainable perspective for the rural sector in Brazil. IEA Bioenergy Task 37, 2013.

MME – Ministry of Mines and Energy (Ministério de Minas e Energia). 2014. Available online at: http://www.mme.gov.br/programas/leiloes_de_energia/menu /inicio.html. Accessed on August 2014.

Moraes, B.S, Junqueira, T.L., Pavanello, P.G., Cavalett, O., Mantelatto, P.E., Bonomi, A., Zaiat, M.. Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? Applied Energy, 113, 825–835, 2014.

Pippo, W.A., Luengo, C. A., Alberteris, L.A.M., Garzone, P., Cornacchia, G. Energy Recovery from Sugarcane-Trash in the Light of 2nd Generation Biofuel. Part 2: Socio-Economic Aspects and Techno-Economic Analysis. Waste and Biomass Valorization, Volume 2, Issue 3, pp 257-266, 2011.

Salomon, K. R., Lora, E. E. S.. Estimate of the electric energy generating potential for different sources of biogas in Brazil. Biomass and Bionergy, 33, 1101 – 1107, 2009.

Thrän et al. Biomethane – status and factors affecting market development and trade. IEA Task 40 and Task 37 Joint Study, 2014.

UDOP - Union of Bioenergy Producers (União dos Produtores de Bioenergia) Indicadores: Consecana. 2014. Available online at: www.udop.com.br. Accessed on August 2014.

Wilkie A.C., Riedesel K.J., Owens J.M. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass Bioenergy, 19, 63–102, 2000.

5. Integrated 1G2G process

In this chapter, the manuscript **"Which enzyme are we looking for? A screening design approach to analyze enzyme influence on the feasibility of second generation ethanol"**, submitted to Biocatalysis and Biotransformation, is presented.

The aim of this study was to identify which variables of enzymatic hydrolysis and enzyme features present significant influence on ethanol production cost. With this purpose, a screening design approach, combined to process simulations and economic assessment, was performed. As a result, a simplified empirical mathematical model was formulated and employed to obtain the set of values for these variables that minimizes ethanol production cost.

Which enzyme are we looking for? A screening design approach to analyze enzyme influence on the feasibility of second generation ethanol

Abstract

Enzymatic hydrolysis is one of the main steps for second generation ethanol production and its operational conditions, such as enzyme loading, solids content and reaction time, significantly impact cellulose conversion to glucose as well as the overall process yield and techno-economic feasibility. Besides, enzyme contribution on ethanol production cost has been pointed out to be underestimated due to little information available. In this work, the influence of enzymatic hydrolysis conditions and enzyme features were studied through a screening design coupled to process simulation and techno-economic assessment of integrated first and second generation (1G2G) sugarcane ethanol production. Hydrolysis yield for each condition was obtained from experimental data; ethanol output and production costs were defined as output responses. This approach allowed a better understanding of the integrated process and the development of a mathematical model for optimization and statistical evaluation. Results showed that the best operating conditions for enzymatic hydrolysis are not necessarily the same when the whole integrated first and second generation process is analyzed. Minimum ethanol production cost,

combining 1G and 2G ethanol, reached US$ 0.42/L for the set of variables determined after optimization.

Keywords: enzyme; ethanol; screening design; process simulation; economic analysis

Introduction

Ethanol from lignocellulosic materials, the so-called second generation (2G) ethanol, has received special attention as an alternative biofuel in the context of reducing dependence on fossil resources and greenhouse gas (GHG) emissions. In Brazil, lignocellulosic materials resulting from sugarcane harvesting and processing – straw and bagasse, respectively – present great potential as feedstock for 2G ethanol production. The utilization of bagasse and 50 % of the available straw has potential to increase approximately 50 % on ethanol production if sugars obtained from cellulose and hemicellulose are efficiently used (Dias et al. 2013).

Since lignocellulosic materials are not directly fermented to ethanol, acid and/or enzymatic hydrolysis is necessary to convert hemicellulose and cellulose fractions into monomeric sugars, e.g. xylose and glucose, respectively (Cardona et al. 2010). Enzymes, in contrast to acid catalysts, are highly specific and allow carrying out a hydrolysis in mild conditions (low pressure and temperature), which reduces costs with chemicals and equipment materials. On the other hand, reaction time in enzymatic hydrolysis can be significantly longer compared to acid hydrolysis.

Besides, Ensinas et al. (2013) have pointed out that the high cost of the enzymes is one of the major problems on 2G ethanol production, thus, its cost should significantly be reduced in order to increase the profitability of an integrated 1G2G ethanol plant. Alternatively, reduction of the amount of enzyme used or its recycle could also benefit process feasibility. However, both process alternatives present a challenge since the dosage of enzymes impacts the yield and rate of the hydrolysis, while the efficiency of hydrolysis can decrease gradually with each recycling step (Sun and Cheng 2002).

Contribution of enzyme cost on 2G ethanol production cost was also discussed by Klein-Marcuschamer et al. (2012). The authors adverted that the inconsistency in the cost of enzymes for biofuel applications impacts techno-economic analysis, and in consequence, adds uncertainties that hinder the decision of researchers and investors to focus efforts and resources and claimed that a realistic cost of enzyme would be around US$ 10.14/kg of enzyme (protein). On the other hand, Humbird et al. (2011) calculated an enzyme cost to be US$ 4.24/kg protein considering on-site production.

Towards the understanding of this issue, this work evaluates the influence of enzymatic hydrolysis conditions and enzyme features through the development of a mathematical model for optimization and statistical evaluation. Mathematical models have been widely used to support decisions for complex problems in industrial environments. A well-adjusted model is capable to predict the process behavior and provides a way to evaluate the impacts of the process parameters and operational conditions on techno-economic impacts, which comes to be a practical and inexpensive way to obtain information about the system (Rivera et al. 2014).

According to a screening design, a series of simulations using the Virtual Sugarcane Biorefinery (VSB), a tool developed at the Brazilian Bioethanol Science and Technology Laboratory (CTBE/CNPEM), were generated for this purpose. The VSB is a novel framework that integrates computer simulation platforms with economic, social, and environmental evaluation tools to assess technical and sustainability indicators of different sugarcane biorefinery alternatives/routes (Cavalett et al. 2012).

Methods

The used approach consisted of a screening design coupled to process simulation and techno-economic assessment of integrated 1G2G ethanol production, using VSB, as can be seen in Figure 1.

The integrated process (depicted in Figure 2) considered an optimized 1G plant – processing 2 million tonnes of sugarcane per year, recovering 50 % of the available straw from the field, with reduced steam consumption and use of efficient 65 bar boilers. For 2G process, it was considered hydrothermal pretreatment and enzymatic hydrolysis, C6 fermentation for ethanol production and biodigestion of C5 to produce biogas used as supplementary boiler fuel. Process simulations were carried out using Aspen Plus®. Table 1 highlights the main technical parameters considered in this work.

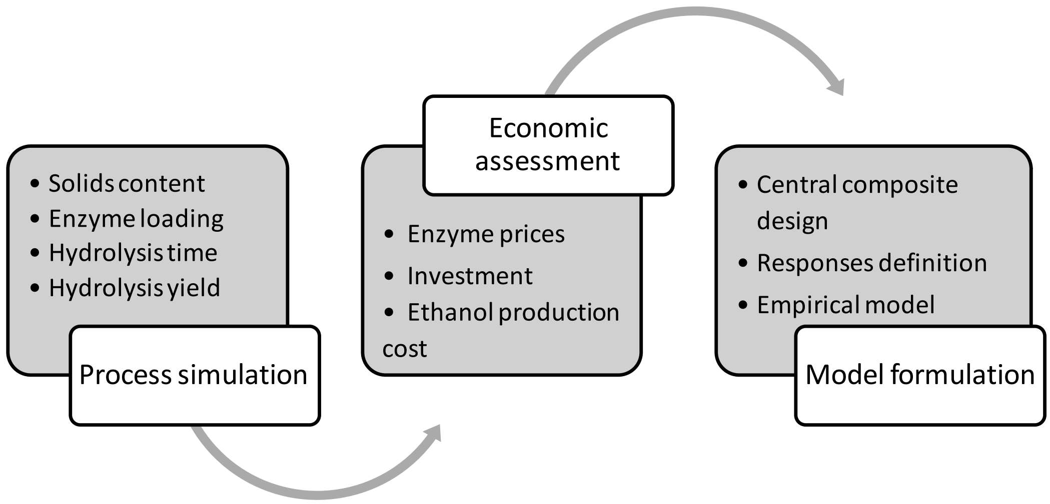

Figure 1: Schematic diagram for the approach and main parameters.

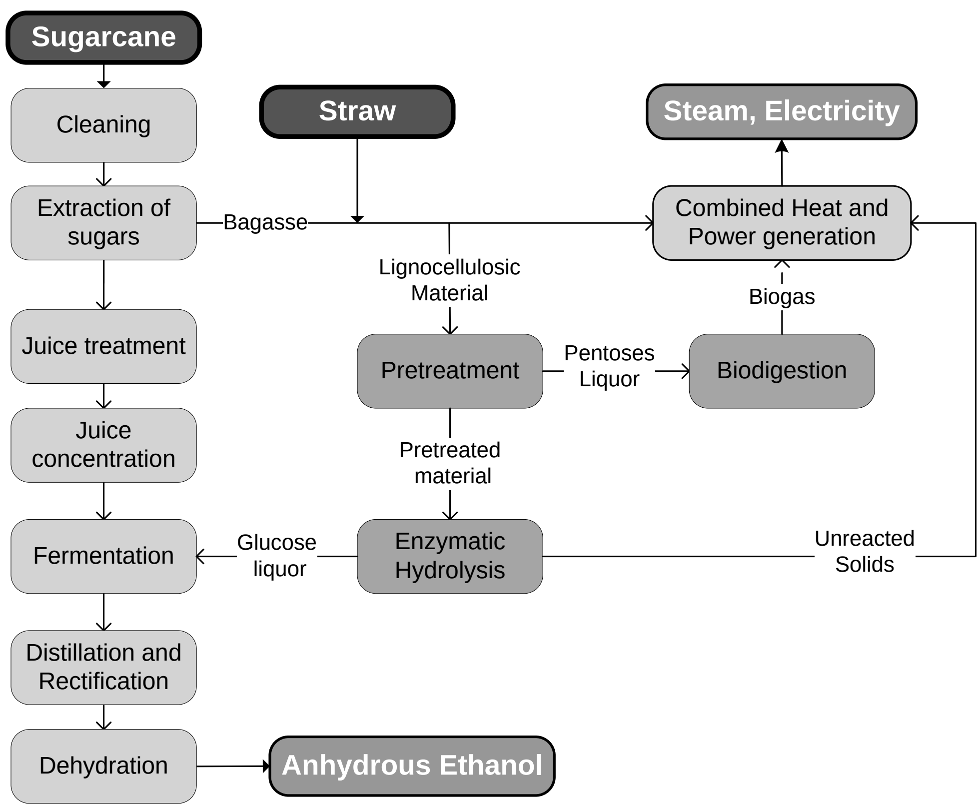

Figure 2: Block flow diagram of integrated 1G2G sugarcane ethanol production.

Table 1: Main process parameters for integrated 1G2G sugarcane ethanol production.

Parameters	**Value**	**Unit**
Season period	200	days
Straw recovered from the field (dry basis)	70	kg/t sugarcane
Efficiency of sugar extraction	96.0	%
Fermentation yield	90.0	%
65 bar boiler efficiency (LHV basis)	87.7	%
COD removal in biodigestion	72.0	%
Electricity consumption – 1G process	30.0	kWh/t sugarcane
Electricity consumption – 2G process	24.0	kWh/t pretreated lignocellulosic material
Pretreatment		
Temperature	190	^oC
Reaction time	10	min
Xylan conversion	91.6	%
Cellulose conversion	9.8	%
Lignin solubilization	12.8	%
Hydrolysis temperature	50	°C

Screening procedure can be performed through Design of Experiments (DOE) techniques, which allows determining the most influential operational variables for each techno-economic response and, therefore, the optimal value for the selected operational variable. This methodology suggests that, before the fitting procedure, it is required to select the values, within the input variables domain, where simulated experiments are conducted (Rivera et al. 2014).

A Central Composite Design (CCD) was used to generate a quadratic model based on 4 variables (enzyme loading, hydrolysis solids content, hydrolysis reaction time and enzyme price). The CCD matrix is composed by sixteen factorial points, eight axial points and one center point, totalizing twenty-five runs. Hydrolysis yield for each condition was obtained from experimental data (de Carli et al. 2012), so levels for each technical variable were defined to match the available data. Enzyme price was based on Klein-Marcuschamer et al. (2012) and Humbird et al. (2011), although it was also included in the assessment a target optimistic value of US$ 2 /kg protein.

Ethanol output and production cost were defined as output responses. Level and value for each input variable are shown in Table 2. The resultant CCD matrix is presented in Table 5 (Appendix) as well as hydrolysis yields for all the runs.

Table 2: Levels and values for input variables in Central Composite Design.

Level	**Enzyme Price*** **(US$/kg protein)**	**Enzyme Loading (FPU/g dry biomass)**	**Hydrolysis Time (h)**	**Solids Content (%)**
Variable name	EP	EL	HT	SC
-2	2	0	0	0.50
-1	4	10	24	5.38
0	6	20	48	10.25
+1	8	30	72	15.13
+2	10	40	96	20.00

* A commercial enzymatic cocktail with a protein concentration of 150 mg/ml, enzyme density and activity equal to 1136 mg/ml and 285 FPU/ml, respectively, was considered.

From process simulation, inputs and outputs flows were used to estimate all expenses and revenues and to size equipment (considering the residence time) in order to calculate the investment. Based on Engineering Economy, a cash flow was projected for each technological scenario. Ethanol production cost was estimated reducing the average market prices of both products – ethanol and electricity – at the same proportion until internal rate of return (IRR) reached zero. In other words, all the expenses (including capital depreciation) were allocated proportionally with respect to the revenue of each product. Table 3 presents market prices for feedstock and products used in this analysis.

Statistical analysis of the data obtained in the screening design was carried out with Statistica™ software package.

Table 3: Prices adopted for the economic analysis (exchange rate US$ 1.00 = R$ 2.16).

Product	Price	Unit	Source
Anhydrous ethanol	0.58	US$/L	Six-years moving average prices for São Paulo state (Jan/2003-Dec/2013) (CEPEA 2014)
Electricity	58.13	US$/MWh	Weighted average of national auctions based on energy from biomass between 2005 and 2013 (ANEEL 2014)
Sugarcane	23.72	US$/t	Six-years moving average prices for São Paulo state (Jan/2003-Dec/2013) (UDOP 2014)
Sugarcane straw	26.20	US$/t	Estimate based on Cardoso et al. (2013), updated to Dec/2013.

Results and discussion

Simulation results for ethanol and electricity outputs vary between 85 and 109 liters per tonne of cane (TC) and 78 and 136 kWh/TC as shown in Figure 3. Since this responses are not dependent on enzyme price, the number of process simulations is lower than number of runs for the screening design approach.

For economic analysis, the investment for each scenario was calculated and its distribution per sector is given on Figure 4. The sector 1G2G (Interface) aggregates 1G plant investment and incremental required investment for inclusion of 2G process on the existing areas: fermentation, distillation, dehydration and combined heat and power generation.

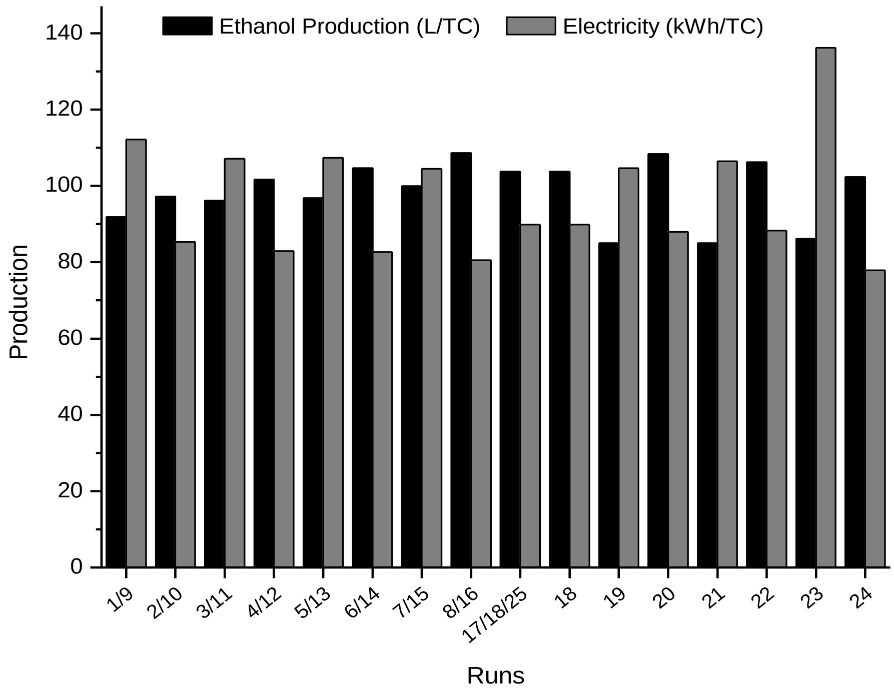

Figure 3: Ethanol and electricity production for the simulated CCD matrix points depicted in the Appendix.

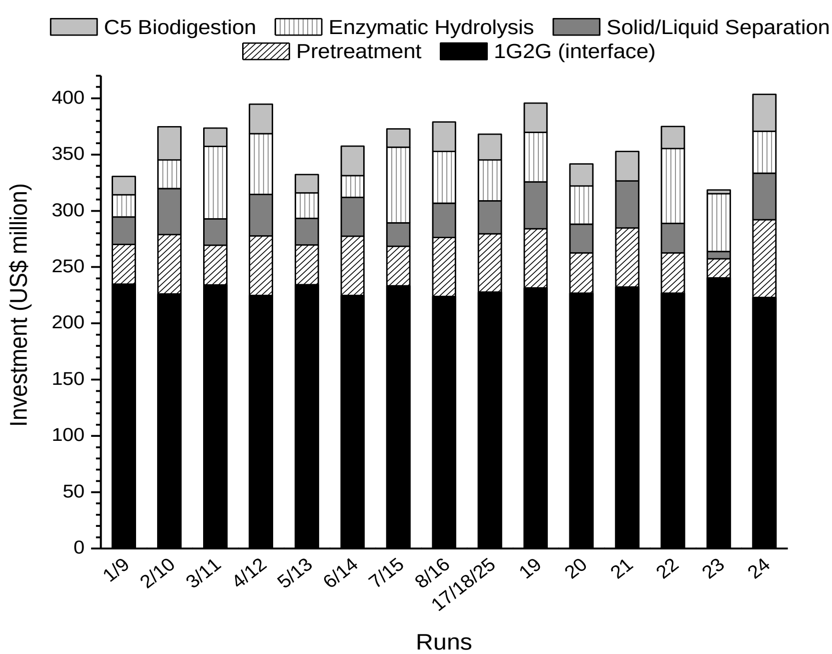

Figure 4: Overall investment and distribution per process section for the simulated CCD matrix points.

As a result of the screening method coupling DOE and VSB simulations, it was possible to obtain simplified mathematical model correlating input variables and combined 1G2G ethanol output (Equation 1) and production cost (Equation 2). Figures 5 to 7 present the effects of the input variables in 1G2G ethanol production cost, based on the model given in Equation 2.

$$\text{Ethanol output (L/TC)}=103.8+0.34X_1^2+3.9X_2-1.4X_2^2+3.1X_3-1.7X_3^2+3.6X_4-2.0X_4^2-0.21X_2X_3+0.69X_2X_4+0.13X_3X_4 \quad (1)$$

$$\text{Ethanol production cost (US\$/L)}=0.463+0.014X_1-0.002X_1^2+0.002X_2+0.0051X_2^2-0.011X_3+0.008X_3^2+0.008X_4+0.004X_4^2+0.006X_1X_2-0.001X_1X_3+0.004X_1X_4-0.003X_3X_4 \quad (2)$$

where X_1, X_2, X_3, and X_4 are the coded values of enzyme price, enzyme loading, hydrolysis time and solids content, as shown in the following equations.

$$X_1=\left(\frac{\text{Enzyme\_Price}-6.0}{2.0}\right) \quad (3)$$

$$X_2=\left(\frac{\text{Enzyme\_Loading}-20.0}{10.0}\right) \quad (4)$$

$$X_3=\left(\frac{\text{Hydrolysis\_Time}-48.0}{24.0}\right) \quad (5)$$

$$X_4=\left(\frac{\text{Solids\_Content}-10.25}{4.875}\right) \quad (6)$$

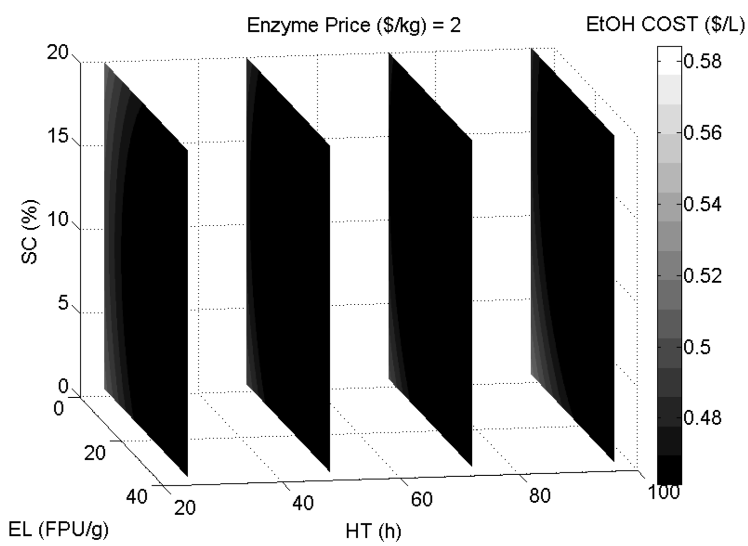

Figure 5: Interactive effects between solids content, enzyme loading and hydrolysis time in 1G2G ethanol production cost for enzyme price equals to US$ 2/kg protein.

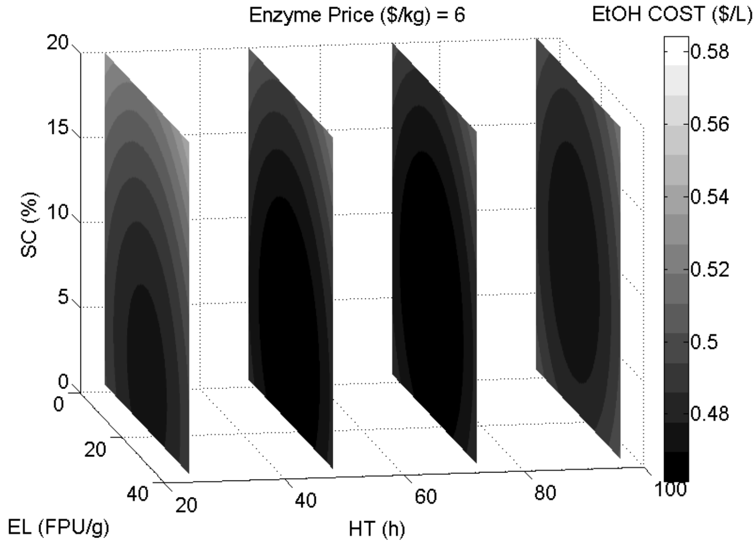

Figure 6: Interactive effects between solids content, enzyme loading and hydrolysis time in 1G2G ethanol production cost for enzyme price equals to US$ 6/kg protein.

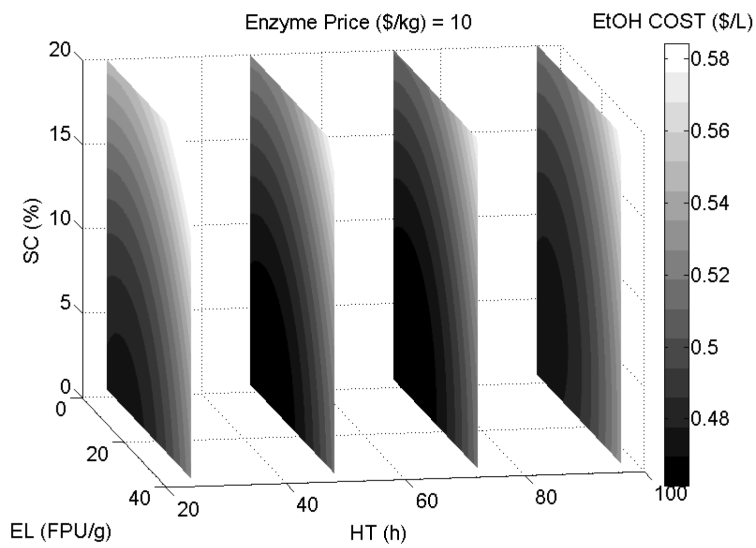

Figure 7: Interactive effects between solids content, enzyme loading and hydrolysis time in 1G2G ethanol production cost for enzyme price equals to US$ 10/kg protein.

From observation of Figure 5, almost all surface area is dark, which shows that it is possible to achieve low ethanol production cost (below $ 0.48/L) in a large range of technical values, since a very low enzyme price is considered. In Figure 6, considering the central value for enzyme price, a delimited area of the surface corresponds to a low ethanol cost, where the increase of hydrolysis time allows the use of higher solids content for medium enzyme loading. Finally, for the superior limit of enzyme price, Figure 7 shows that a reduction on enzyme loading and on solids content is required to reach low ethanol production cost.

Also based on Equation 2, the set of values for the input variables that provides the lowest ethanol production cost was determined. Optimal values were US$ 2/kg protein for enzyme price, enzyme loading of 30.6 FPU/g dry biomass, 62.8 hours of hydrolysis and solids content of 11.0 %, resulting in a combined 1G2G ethanol production cost of US$ 0.42/L (5 % higher than 1G ethanol production cost – US$ 0.40/L). Using Equation 1, the total amount of ethanol produced (109.3 L/TC) was calculated, which corresponds to a 30 % increase in ethanol production when compared to a 1G plant that produces 84.8 L/TC.

Since there are some uncertainties related to enzyme price and the minimum value for this variable (US$ 2/kg protein) is difficult to achieve, the calculated minimum ethanol production costs for fixed enzyme prices are organized in Table 4.

The production cost for 2G ethanol was calculated considering that the combined 1G2G production cost is the average, weighted by the production, between 1G and 2G ethanol.

Table 4. Optimum set of values for minimum ethanol production cost (MEPC) and calculated enzyme contribution for fixed enzyme prices.

EP (US$/kg protein)	EL (FPU/g dry LCM[1])	HT (h)	SC (%)	Ethanol Output (L/TC)	MEPC 1G2G (US$/L)	MEPC 2G (US$/L)	Enzyme (US$/L E2G[2])
2	30.6	62.8	11.0	109.3	0.42	0.49	0.15
4	24.7	61.2	8.4	105.0	0.44	0.61	0.24
6	18.8	59.7	5.9	99.6	0.46	0.80	0.30
8	12.9	58.1	3.4	93.2	0.46	1.07	0.33
10	6.9	56.5	0.8	85.8	0.46	5.55	0.77

[1] LCM refers to the amount of pretreated lignocellulosic material.

[2] E2G – second generation ethanol.

From Table 4, it can be seen that higher enzyme prices led to reductions on enzyme loading and solids content to achieve the minimum ethanol production cost. Although ethanol production cost is the same for enzyme prices higher than US$ 6/kg protein, ethanol output is significant lower, and for the highest enzyme price, it is similar to 1G ethanol output. The reduction of 2G ethanol production is justified by low solids content implying in extremely high energy consumption, reducing the amount of lignocellulosic material available for 2G. It means that 2G ethanol production is not attractive for higher enzyme prices when a low ethanol production cost is aimed. Considering the upper limit for enzyme price (US$ 10/kg protein), 2G ethanol production cost would be more than ten-fold the 1G production cost; this fact is consequence of the very low solids content (0.8 %) and low yield on hydrolysis due to reduced enzyme loading motivated by its high price.

It is worthwhile to mention that these optimal values are significantly dependent on experimental data and assumptions, thus it should not be extrapolated to other cases without applying the methodological approach to generate a new and representative correlation model.

Conclusions

This approach allowed a better understanding of the integrated process as well as the development of a mathematical model for optimization and statistical evaluation. An empirical model was formulated to predict 1G2G ethanol production cost and used to determine optimal conditions (lower ethanol production cost). In addition, contour plots were presented, allowing to visually identify the range of values that provides optimal results.

In addition, the methodology presented in this work can be easily applied to other processes in order to find a correlation that takes into account technical and economic parameters. For the integrated 1G2G ethanol production process, it is particularly useful, since the best operating conditions for enzymatic hydrolysis are not necessarily the same when the whole process is taken into account.

Appendix: The Central Composite Design matrix.

Table 5: Central Composite Design matrix and hydrolysis conversions for each run.

Run	Input Variables				Hydrolysis conversions (%)		
	Enzyme price (US$/kg protein)	Enzyme loading (FPU/g dry biomass)	Hydrolysis Time (h)	Solids content (%)*	Cellulose to Glucose	Cellulose to Oligomers	Xylan to Xylose
1	8.75	10	24	5.38	32.1	1.2	42.3
2	8.75	10	24	15.13	30.0	1.1	39.9
3	8.75	10	72	5.38	52.4	1.6	54.2
4	8.75	10	72	15.13	44.1	2.0	50.3
5	8.75	30	24	5.38	55.6	2.0	52.0
6	8.75	30	24	15.13	53.4	2.3	56.0
7	8.75	30	72	5.38	72.6	2.3	69.4
8	8.75	30	72	15.13	69.0	3.4	71.9
9	16.25	10	24	5.38	32.1	1.2	42.3
10	16.25	10	24	15.13	30.0	1.1	39.9
11	16.25	10	72	5.38	52.4	1.6	54.2
12	16.25	10	72	15.13	44.1	2.0	50.3
13	16.25	30	24	5.38	55.6	2.0	52.0
14	16.25	30	24	15.13	53.4	2.3	56.0
15	16.25	30	72	5.38	72.6	2.3	69.4
16	16.25	30	72	15.13	69.0	3.4	71.9
17	5.00	20	48	10.25	61.8	2.4	67.1
18	20.00	20	48	10.25	61.8	2.4	67.1
19	12.50	0	48	10.25	0.0	0.0	0.0
20	12.50	40	48	10.25	82.0	3.5	86.5
21	12.50	20	0	10.25	0.0	0.0	0.0
22	12.50	20	96	10.25	73.0	3.1	81.2
23	12.50	20	48	0.50	51.5	1.1	44.5
24	12.50	20	48	20.00	41.5	1.8	46.3
25	12.50	20	48	10.25	61.8	2.4	67.1

* Levels for solids content corresponding to 5.38, 10.25, 15.13 % considered original experimental data for 5, 10 and 20 % solids.

References

ANEEL - Brazilian Electricity Regulatory Agency (Agência Nacional de Energia Elétrica) [online] Available at: http://www.aneel.gov.br. Accessed on 20 March 2014.

Cardona CA, Quintero JA, Paz IC. 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresource Technol 101:4754-4766.

Cardoso TF, Cavalett O, Chagas MF, Morais ER, Carvalho JLN, Franco HCJ, Galdos MV, Scarpare FV, Braunbeck OA, Cortez LAB, Bonomi A. 2013. Technical and economic assessment of straw recovery in the sugarcane bioenergy production system. Sci Agric 70:353-360.

Cavalett O, Junqueira TL, Dias MOS, Jesus CDF, Mantelatto PE, Cunha MP, Franco HCJ, Cardoso TF, Maciel-Filho R, Rossell CEV, Bonomi A. 2012. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. Clean Technol Envir 14:399–410.

CEPEA - Center for Advanced Studies on Applied Economics (Centro de Estudos Avançados em Economia Aplicada) [online] Available at: http://cepea.esalq.usp.br/english. Accessed on 20 March 2014.

de Carli CM, Pradella JGC, Delabona PS. 2012. Enzymatic hydrolysis of sugarcane bagasse: a analysis [Hidrólise enzimática de bagaço de cana-de-açúcar: uma análise]. In: X Seminário Brasileiro de Tecnologia Enzimática - ENZITEC 2012.

Dias MOS, Junqueira TL, Rossell CEV, Bonomi A, Maciel-Filho R. 2013. Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane. Fuel Process Technol 109:84-89.

Ensinas AV, Codina V, Marechal F, Albarelli J, Silva MA. 2013. Thermo-economic optimization of integrated first and second generation sugarcane ethanol plant. Chem Eng Trans 35:523-528.

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. Available at: http://www.osti.gov/bridge. Accessed on 23 January 2013.

Klein-Marcuschamer D, Oleskowicz-Popiel P, Simmons BA, Blanch HW. 2012. The Challenge of Enzyme Cost in the Production of Lignocellulosic Biofuels. Biotechnol Bioeng 109:1083-1087.

Rivera EC, Geraldo VC, Sanghikian N, Junqueira TL, Capitani DHD, Jesus CDF, Maciel- Filho R, Bonomi A. 2014. A Screening Design to Analyze the Influence of Technological Configurations on Techno-economic Parameters for Autonomous Distilleries in Brazil. Chem Eng Trans 37:307-312.

Sun Y, Cheng J. 2012. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technol 83:1-11.

UDOP- Union of Bioenergy Producers (União dos Produtores de Bioenergia). Available at: http://www.udop.com.br/cana/tabela_consecana_saopaulo.pdf. Accessed on 20 March 2014.

6. Alternatives for extending operation in biorefineries

The manuscript **“Process configurations and feedstock alternatives to extend the operational period of sugarcane biorefineries”** assesses year-round electricity production considering the storage of lignocellulosic material for operation of cogeneration system in the off-season as well as alternatives to also extend ethanol production period. These alternatives include concentration and storage of sugarcane juice, use of sweet sorghum as drop-in feedstock and integration of 2G process.

Process configurations and feedstock alternatives to extend the operational period of sugarcane biorefineries

Abstract

Unlike most industrial facilities, sugarcane biorefineries operate from 6 to 8 months per year, since it is usually limited by the sugarcane harvesting period. In addition, sugarcane cannot be stored for more than a few days due to feedstock degradation, so that industrial facility is idle in the remaining months. As a result, costs related to investment on equipment as well as those due to the feedstock are the most important contributions on ethanol production cost and these should be considered in any strategy to extend operational period. In this work, four alternatives to extend the operational period were evaluated: (1) production of electricity all year-round using stored bagasse and straw; (2) use of concentrated juice for ethanol production in the off-season; (3) sweet sorghum processing in the off-season to produce ethanol and electricity; (4) integration of second generation plant processing all year-round. These are options, in principle, possible to be implemented in existing plants. Scenarios were compared to the Base Case – an autonomous distillery producing ethanol and electricity only in the harvest period – considering techno-economic aspects, such as ethanol and electricity production, internal rate of return (IRR) and net present value (NPV). Scenarios 1 and 2 presented ethanol production similar to Base Case, because no additional sugar source was considered. An increase of 10 and 35 % was obtained including operation with sweet sorghum (from sugarcane replanting area) and second generation ethanol process, respectively. All alternative scenarios equaled or exceeded economic profitability of the Base Case. Scenario 2 enabled year-round production of ethanol and electricity with lower investment than Base Case. Scenarios 1 and 3 were more economically attractive, presenting higher IRR. Scenario 4 presented a NPV comparable to Scenarios 1 and 3, but lower IRR, mainly due to the high investment required for second generation process.

Keywords: Ethanol; sugarcane; extended operation; sweet sorghum; second generation process

Introduction

Sugarcane cannot be stored for more than a few days due to degradation and mills usually operate only during the harvest period. Sugarcane harvest periods vary according to rainfall to allow cutting and transportation operations while reaching the best maturation point and maximizing sugar accumulation (CGEE and BNDES, 2008). In the Center-South region of Brazil, where most mills are located, sugarcane harvest, and consequently, mills operation goes from April to November (Souza and Macedo, 2010), that means around 8 months.

One alternative to reduce idle capacity of the plant is the production of electricity all year-round. Cogeneration system, which produces steam and electricity, constitutes 30 to 35 % of costs with equipment in a sugarcane biorefinery (based on data from Souza and Macedo, 2010). Large surplus of electricity can be generated, especially in plants with low steam demand and efficient cogeneration system (using high pressure boilers and extraction-condensing turbines).

However, the main challenge is to produce ethanol all year-round. More prolonged periods of operation are desirable towards a better use of existing production capacity and minimization of storage during the intercrop period. For instance, by extending the harvest period from 150 days to 200 days (33 % increase), the tank storage capacity required to meet a constant demand would be reduced in 23 % (CGEE and BNDES, 2008).

Regarding ethanol production, three alternatives for extended operation may be envisioned: concentration and storage of inverted sugarcane juice (high test-molasses), use of other feedstock based on sugars or starch (e.g., sweet sorghum, beet and corn) and integration with second generation ethanol production using lignocellulosic materials (e.g. sugarcane bagasse and straw, forest residues, biomass sorghum).

The use of concentrated juice presents as advantage the fact that does not rely on the use of other feedstock, which could need some adaptation on harvesting, handling and processing, but requires higher steam consumption and additional investment on evaporation process and storage of concentrated juice that will be processed in the sugarcane off-season. On the other hand, reductions of investment on fermentation, distillation and dehydration processes as well as on ethanol storage are expected.

Some studies have been carried out considering sweet sorghum as complementary feedstock along with sugarcane (Cavalett et al., 2013; Cutz and Santana, 2014). Sweet sorghum has already been used by some mills in a demonstration stage, employing the same equipment for harvesting as well as operating milling and processing without any adaptation of the sugarcane biorefinery (Ceres, 2014a). Besides, sweet sorghum can be produced in the sugarcane replanting areas, yielding extra feedstock without interfering in the sugarcane production cycle (Cavalett et al., 2013). Cutz and Santana (2014) evaluated the use of sweet sorghum in Central America in sugarcane mills and concluded that its processing during off-season in sugarcane biorefineries improves profitability as both ethanol and electricity production increase.

Corn, the main feedstock for ethanol production in United States, has been considered a potential alternative for integration with sugarcane in Brazil as its availability increased due to the corn-soybean rotation in the Center-West region. Milanez et al. (2014) assessed different integration scenarios of corn and sugarcane and showed that there is potential to increase in 10 % the amount of ethanol produced in Brazil without planting more sugarcane and building new mills; however better economic performance is achieved with low corn prices and high demand for animal feed (corn ethanol co-product).

The use of lignocellulosic material to produce ethanol (so-called second generation process) is especially attractive since it does not compete with food crops and is less expensive than conventional agricultural feedstock (Alvira et al., 2010). In Brazil, the abundance of feedstock near the processing site must be taken into account, as low-density biomass involves significant handling and transportation costs; thus sugarcane bagasse and straw are obvious choices. Other agricultural by-products include corn straw, wheat straw, rice straw and hulls, grass, forestry materials and residues from citrus, coconut and cassava processing (Ferreira-

Leitão et al., 2010). In the case that second generation ethanol production process is integrated to a first generation plant, it is possible to share part of the infrastructure, such as juice concentration, fermentation, distillation and cogeneration system.

In this work, four alternatives to extend operational period of sugarcane biorefineries are assessed: (1) production of electricity all year-round using stored bagasse and straw; (2) use of concentrated juice for ethanol production in the sugarcane off-season; (3) sweet sorghum processing in the sugarcane off-season to produce ethanol and electricity; (4) integration of second generation plant processing all year-round. The Virtual Sugarcane Biorefinery – an integrated assessment tool developed by Brazilian Bioethanol Science and Technology Laboratory (CTBE) – was employed to perform techno-economic analysis, showing impacts of each alternative when compared to an autonomous distillery plant that produces ethanol and electricity only in the harvest period.

Evaluation Procedure

Scenarios Description

Base Case

As a Base Case scenario, the first generation ethanol production process is represented by an optimized autonomous distillery, with process improvements aiming at reducing steam consumption and increasing electricity surplus, using straw (50 % of the amount produced in the field), molecular sieves for dehydration, high pressure boilers (65 bar) and extraction-condensing turbines. This plant has a processing capacity of 2 million tonnes of sugarcane per year, operating 200 days per year, producing anhydrous ethanol and electricity. Main process steps are presented in Figure 1. Operating and process parameters for a typical Brazilian sugarcane biorefinery were obtained in the literature (CTBE, 2012).

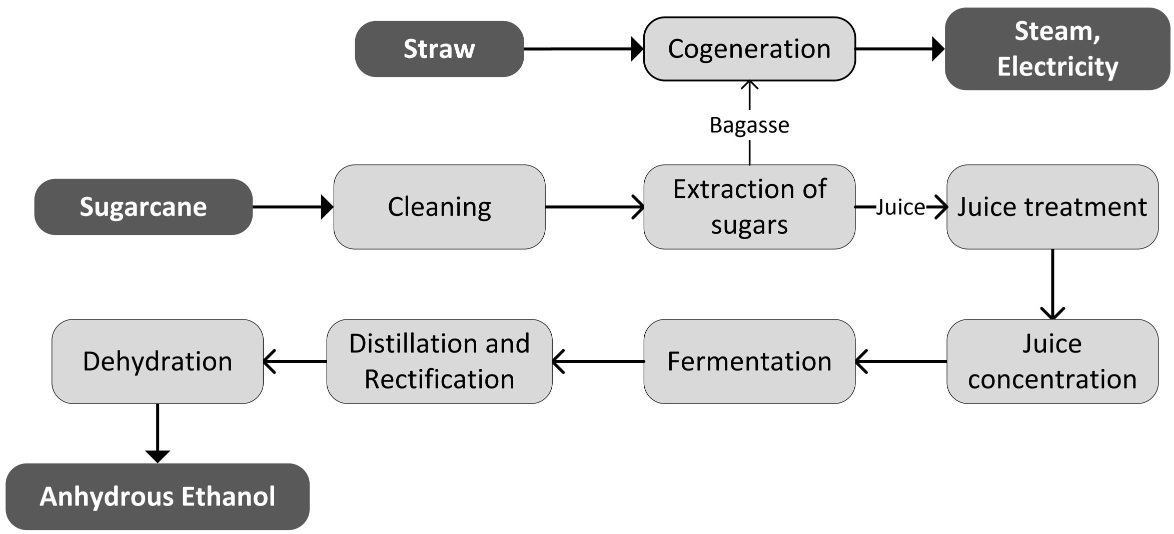

Figure 1. Block flow diagram for an autonomous distillery.

Scenario 1

The first scenario consists in the production of electricity all year-round (330 days) using stored bagasse and straw. The amount of material that can be stored during the season depends on steam consumption of the autonomous distillery, which is approximately 340 kg per tonne of cane (TC) due to the optimization considerations earlier addressed.

In order to minimize idle capacity, it was defined that the same amount of fuel (bagasse and straw) would be burnt in the boiler in both periods (season and off-season). In the season, part of generated steam is not consumed in the process and is used to generate electricity in extraction-condensing turbines; in the off-season, since there is almost no need of steam, electricity generation is maximized and all steam produced is expanded/condensed. Since off-season period (130 days) is shorter than season (200 days), the amount stored per hour is lower than the amount burnt in the boilers. The consideration that 50 % of straw is recovered from the field and used as fuel allows reaching this balance. It was considered that electricity demand during the season is 30 kWh/TC and that it is not significant in the off-season.

Commonly, sugarcane mills have more than one piece of equipment with the same function. Particularly with the introduction of straw, larger capacity in the cogeneration system will be required. Therefore, the plant can be designed in such a way that some turbines operate at full capacity and one turbine (e.g., a back pressure turbine) is idle in the off-season period. For this reason, no reduction on turbines efficiency was considered for off-season operation.

Scenario 2

The second scenario consists in the production of ethanol and electricity all year-round (330 days) using stored bagasse, straw and concentrated juice.

In this scenario, the same amount of sugarcane is crushed, producing sugarcane juice and bagasse; the latter is mixed to straw, being a fraction burnt in the boilers and the remaining stored to supply steam and electricity in the off-season. Similar to scenario 1, it was defined that the same amount of fuel (bagasse and straw) would be burnt in the boiler in both periods (season and off-season).

In order to store concentrated juice, it is necessary to invert sucrose to prevent sugars crystallization and degradation. Treatment of sugarcane juice is carried out in the same way as Base Case, but concentration is performed using a 5-stage multiple effect evaporator. The juice is concentrated up to 18 % soluble solids in the first evaporation stage; part of this juice is sent to fermentation (resulting in an wine content of 8.5 % v/v) and the remaining is further concentrated. Inversion of sucrose is carried out adding *Saccharomyces Cerevisiae* – yeast conventionally used in the fermentation process – in the concentrated juice (around 53% soluble solids) (CHEN; CHOU, 1993). The inverted juice is finally concentrated up to 85 % soluble solids, producing the high test molasses (HTM).

The proportion of the juice destined to off-season operation (130 days) was defined in such a way that the feed of fermentation was the same all year-round (330 days). For this reason, equipment capacities from fermentation to ethanol dehydration and storage are smaller than those of Base Case and are better used, reducing idle capacity. Cogeneration sector is also smaller than Base Case and operates all year-round with full capacity.

Scenario 3

Unlike previous scenarios, scenario 3 considers another feedstock besides sugarcane and straw: sweet sorghum (*Sorghum bicolor L.*). In this work, the variety BRS511 of sweet sorghum from the Brazilian Agricultural Research Corporation (Parrella and Schaffert, 2012) was considered. This variety contains about 11.1 % fibers, 10.6 % sucrose, 1.0 % reducing sugars and 74.5 % moisture.

It was considered that sweet sorghum would be processed in the off-season to produce ethanol and electricity, using the same industrial equipment, considering the efficiencies shown in Table 1. Sugarcane processing efficiencies are also shown for reference. Sweet sorghum bagasse is burnt in the boilers, considering the same efficiency as sugarcane bagasse, providing the required steam and electricity in the off-season, so there is no need to store bagasse and straw.

Table 1. Efficiencies for ethanol production process using sugarcane and sweet sorghum as feedstock.

Parameters	**Sugarcane**	**Sweet sorghum**
Efficiency of sugars extraction	96 %	90 % [a]
Sucrose content in the filter cake [b]	1 %	3 % [a]
Fermentation efficiency	90 %	88 % [c]
Distillation efficiency	99 %	99 % [c]

[a] Values based on Pacheco (2012);

[b] Represents the losses on juice treatment;

[c] It was assumed that fermentation efficiency would be lower for sweet sorghum processing due to possible presence of inhibitors, but distillation efficiency would not be affected.

This scenario considered two sub-scenarios:

(3A) Sweet sorghum from sugarcane replanting areas (around 20 % of the area), is enough to extend the season 28 days per year of operation at full scale, considering the same hourly processing of sugarcane (417 t/h);

(3B) Sweet sorghum is not restricted to sugarcane replanting areas and can be purchased from independent producers to operate 60 days in the off-season. A longer period can be considered, but it is dependent on climate conditions of each region (Ceres, 2014b).

Scenario 4

An integrated first and second generation ethanol production process from sugarcane bagasse and straw, as illustrated in Figure 2, is evaluated in this scenario.

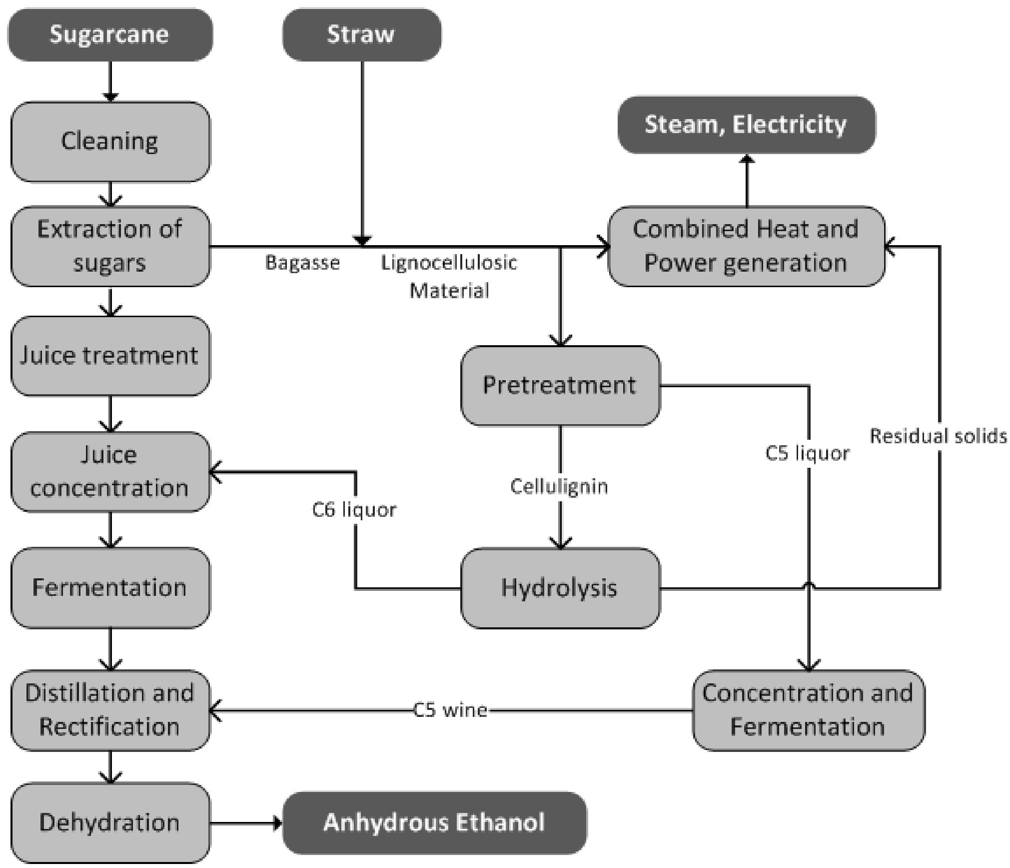

Figure 2. Block flow diagram for an integrated first and second generation process.

Since other process steps (e.g. pretreatment and hydrolysis) are required to make available fermentable sugars from lignocellulosic material, it was assumed that second generation (2G) process would operate all year-round (330 days), allowing a better use of equipment. Therefore, part of the lignocellulosic material (bagasse and straw) is stored for off-season operation (130 days). This proportion was defined in such a way 2G process would have the same feed in pretreatment stage all year-round. Part of cogeneration system is used, but there is still idle capacity since steam consumption is much lower in the off-season when compared to season.

For 2G process, catalyzed steam explosion pretreatment and enzymatic hydrolysis were considered, assuming optimistic figures (Pereira et al., 2014). Process conditions and yields are presented in Table 2. Residues from hydrolysis (rich in lignin) are burnt together with a part of the bagasse and straw for steam and electricity generation to meet process energy requirement.

Table 2. Process conditions and yields for second generation process (based on Pereira et al., 2014).

Parameters	**Value**
Pretreatment	
Temperature (°C)	150
Residence time (min)	10
Sulphuric acid addition (wt%)	0.5
Conversion of xylan to xylose (%)	65
Xylan degradation into furfural (%)	10
Conversion of cellulose to glucose (%)	5
Cellulose degradation into hydroxymethylfurfural - HMF (%)	1.5
Enzymatic hydrolysis	
Temperature (°C)	50
Residence time (h)	48
Solids content (%)	15
Enzymatic load (FPU/g dry lignocellulosic material)	10
Conversion of cellulose into glucose (%)	70
Conversion of xylan into xylose (%)	35
Fermentation – glucose conversion into ethanol (%)	90
Fermentation – pentoses conversion into ethanol (%)	80

Scenarios simulation and evaluation

Process simulation was carried out using Aspen Plus®, considering the methodology described in CTBE (2012). Mass and energy balances provided information to estimate investment as well as operating costs and revenues required for economic analysis.

Economic analysis was based on a cash flow analysis for a project lifetime of 25 years, considering 2 years for construction and start-up of the plant. Linear depreciation (10 % per year) is assumed as well as no salvage value of equipment at the end of the lifetime period. Tax rate (income and social contributions) was assumed as 34 %. Internal rate of return (IRR) and net present value (NPV) for each alternative were calculated and compared to the values obtained for the Base Case. Minimum acceptable rate of return (MARR) was defined as 12 %.

Fixed capital investment for optimized autonomous distillery (Base Case) was estimated based on data and methodology presented in CTBE (2012). Investment was calculated as a function of the main flows (e.g. processed sugarcane, production of ethanol and steam) for each processing area, using a cost capacity exponent equal to 0.6. Since all scenarios were analyzed as new installations (greenfield projects), this approach allowed to estimate reduction/increase of investment for each area according to flows obtained through process simulation.

Main assumptions for each scenario are described as follows:

- Scenario 1: investment of cogeneration section (steam and electricity generation area) was re-calculated considering steam production obtained for this scenario. Other areas were not affected when year-round operation was assumed only for cogeneration. No additional costs or losses were considered due to storage of bagasse and straw (outdoor deposition);

- Scenario 2: investment on distillery was subdivided into juice treatment (20 %), fermentation (35 %) and distillation/dehydration/storage (45 %), so that juice treatment would not be affected in this scenario and investment in the remaining stages could be estimated. Investment of cogeneration section was also re-calculated considering steam production of Scenario 2. Investment for inclusion of multiple effect evaporation and storage of concentrated juice (around 5000 m^3) were also estimated;

- Scenario 3: investment was considered to be the same as Base Case, since no additional equipment are required for sweet sorghum processing (“drop-in” feedstock);

- Scenario 4: investment for 1G plant and processing areas shared between 1G and 2G processes – such as fermentation, distillation, dehydration, storage and cogeneration – were estimated using the same assumptions for autonomous distillery and the cost-capacity equation. For 2G equipment, the approach was based on the main equipment cost (e.g., pretreatment and hydrolysis reactors), considering an installation factor around 2.9.

Feedstock costs and products prices considered in this analysis are presented in Table 3.

Table 3. Feedstock costs and products prices (exchange rate US$ 1.00=R$ 2.29).

Product	Historical Average	Observations
Sugarcane (US$/t) - 70 % moisture	24.04	Prices for São Paulo State (UDOP, 2014), from Aug/2005 to Jul/2014
Sugarcane straw (US$/t) – 15 % moisture	29.55	Estimated based on 50 % straw recovery through baling system (Cardoso et al., 2013)
Sweet sorghum (US$/t) – 74.5 % moisture	21.07	Estimated based on NovaCana.com (2013), updated to Jul/2014
Enzyme (US$/kg protein)	6.00	Value assumed, considering activity of 2 FPU/mg of protein
Anhydrous ethanol (US$/L)	0.59	Prices for São Paulo State (CEPEA, 2014), from Aug/2005 to Jul/2014
Electricity (US$/MWh)	57.83	Prices for electricity from sugarcane bagasse in national auctions (MME, 2014), from 2005 to 2013

Note: No price differentiation was considered for electricity or ethanol produced in the off-season period, even in the case of second generation ethanol.

Results and discussion

Main flows and products for each scenario, based on process simulation results, are presented in Table 4.

The information provided in Table 4 was used to elaborate Figure 3. From this figure, it can be observed that the annual production of ethanol is the same for Base Case and Scenarios 1 and 2, although electricity production is lower in Scenario 2 due to higher steam consumption in evaporation of sugarcane juice. In the case of using sweet sorghum as a complementary feedstock, 10 and 20 % increase on ethanol production is obtained, while electricity surplus raises 5 and 10 % in Scenarios 3A and 3B, respectively. Integrated 1G2G ethanol process allows producing 35 % more ethanol, without using additional feedstock, but decreases electricity production in almost 60 %.

Table 4. Main flows and products for each scenario.

Parameter	Base Case	Scenario 1	Scenario 2	Scenario 3 (A/B)	Scenario 4
Sugarcane processed (MTC/year)	2.0	2.0	2.0	2.0	2.0
Source for ethanol production – off-season	-	-	Concentrated juice (HTM)	Sweet sorghum (SS)	Bagasse+ straw (LCM*)
Reference flow – off-season (t/h)	-	-	HTM: 57.9	SS: 416.7	LCM: 26.6 (dry basis)
Specific ethanol production – off-season	-	-	443.9 L/t HTM	61.4 L/t SS	294.1 L/t LCM
Operating days – off-season	-	130	130	3A: 28 3B: 60	130
Ethanol produced –season (m^3/h)	35.4	35.4	21.4	35.4	43.2
Ethanol produced – off-season (m^3/h)	-	-	21.4	25.6	7.5
Steam produced –season (t/h)	389.1	235.8	235.8	389.1	234.2
Steam produced – off-season (t/h)	-	235.8	235.8	207.1	62.9
Surplus electricity – season (MW)	81.3	38.4	41.0	81.3	27.5
Surplus electricity – off-season (MW)	-	65.4	55.1	28.6	9.4

* LCM means lignocellulosic material and is defined in this work as the amount of bagasse and straw processed in the 2G process.

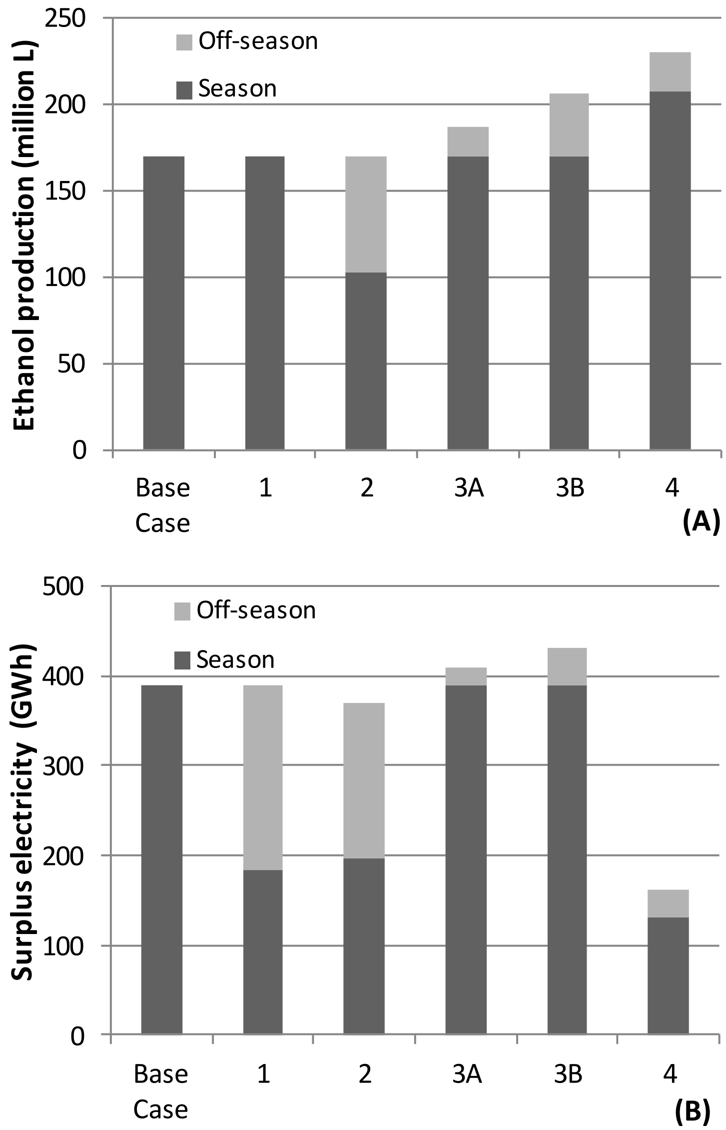

Figure 3. Annual production of ethanol (A) and surplus electricity (B) for each scenario evaluated.

Based on the assumptions described in the Methods section, fixed capital investment was calculated for each scenario (Figure 4). Investment values were lower for Scenarios 1 and 2, due to the reduction on equipment capacity resulting from the larger period of operation. As stated before, no additional investment was assumed for scenarios that process sweet sorghum. A significant increment on investment was observed when 2G process was integrated to the distillery, though investment on cogeneration was reduced, total investment was considerably higher when compared to the other scenarios.

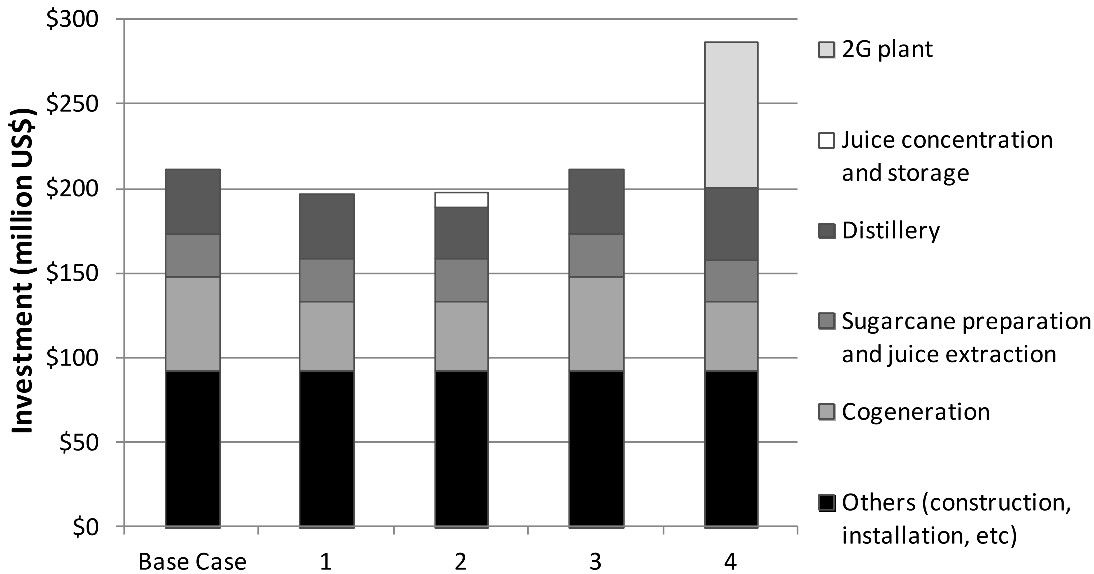

Figure 4. Distribution of investment per area of the plant.

Economic analysis was carried out in order to compare the alternatives, based on internal rate of return and net present value. Results are illustrated in Figure 5.

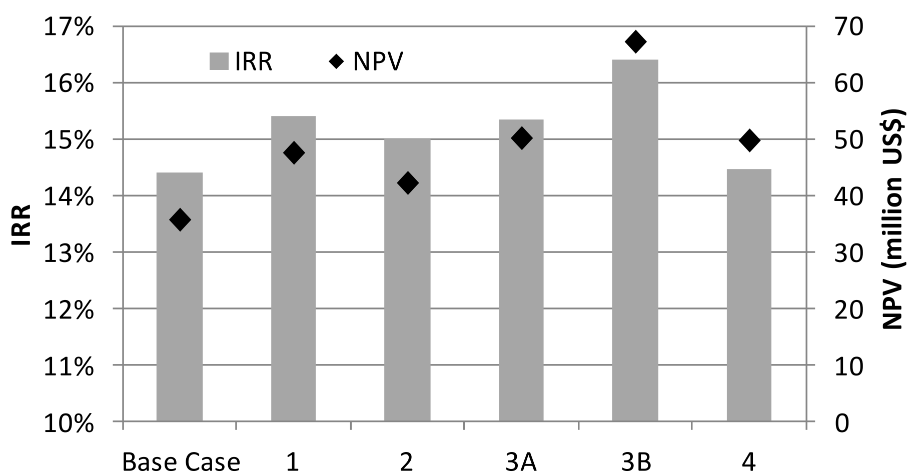

Figure 5. Internal rate of return (IRR) and net present value (NPV) for the evaluated scenarios.

All alternative scenarios are equal or even exceed Base Case in terms of economic profitability. Scenario 2, although presents higher IRR and NPV compared to the Base Case, does not seem an economically attractive alternative, since it has similar ethanol production and investment when compared to Scenario 1, but has a lower electricity surplus, which decreases IRR.

Processing sweet sorghum enabled to increase both IRR and NPV and, considering that it is possible to operate 60 days in the off-season, Scenario 3B is the most promising scenario among evaluated alternatives. Since the market for sweet sorghum is not yet established, a sensitivity analysis was performed for Scenario 3B, assuming a ± 20 % variation on sweet sorghum costs. The IRR for Scenario 3B would increase to 17.2 % (in the -20 % case) and decrease to 15.6 % (in the +20 % case), but would still be higher than other evaluated scenarios.

Although results for sweet sorghum showed its great potential as complementary feedstock, the adaptation of the machinery for an efficient harvesting, definition of a strategy for planting and advance on the learning curve are some challenges to be overcome with experience gathered each year (NOVACANA, 2013).

Regarding integrated 1G2G process (Scenario 4), IRR was similar to Base Case, but NPV was significantly higher, which shows that it has potential to be implemented. Although its IRR is lower than those of Scenarios 1 and 3A, NPV was comparable, which shows that high investment cost is significantly affecting economic feasibility of 2G process. It is expected that, advancing on the 2G learning curve, gains on ethanol productivity and lower operating and capital costs will be achieved.

Conclusions

In this work, alternative scenarios for extending the operational period of an autonomous distillery were evaluated. This operational period is usually limited by the sugarcane harvesting period; thus, these industrial facilities are idle during off-season. Definition of scenarios included all-year round operation for cogeneration system and, in some cases, all-year round ethanol production.

Economic assessment showed that plants can benefit from extension of cogeneration system operational period, since this area represents a considerable fraction of investment cost.

On the other hand, storage of sugarcane juice concentration to produce ethanol during off-season was less advantageous than operating only cogeneration system all year-round.

Sweet sorghum as a drop-in feedstock has potential advantages to increase the operational period. However, there are still some uncertainties regarding its agricultural and industrial productivities. More information should be available soon due to the increasing number of tests being performed with this alternative feedstock in the sugar-energy sector. Besides, considering sweet sorghum from independent producers introduces issues about logistics and transportation, since, in nowadays production model, most of area around sugarcane mills are dedicated to sugarcane.

Production of all year-round second generation ethanol using surplus bagasse and straw available in the autonomous distillery was also evaluated. Even sharing part of the infrastructure, investment cost of the integrated 1G2G plant was considerably higher than other scenarios. Since second generation technology is still in a development stage, with just a few plants being installed in Brazil in a demonstration stage, improvement on productivities as well as reduction of operating and capital costs are expected in the next few years.

References

Alvira, P., Tomás-Pejó, E., Ballesteros, M., Negro, M. J. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. Bioresour. Technol. 101, 4851–4861, 2010.

BNDES and CGEE (Coord.). Sugarcane-Based Bioethanol – Energy for Sustainable Development, Rio de Janeiro: BNDES, 2008.

Cardoso, T. F., Cavalett, O., Chagas, M. F., Morais, E. R., Carvalho, J. L. N., Franco, H. C. J., Galdos, M. V., Scarpare, F. V., Braunbeck, O. A., Cortez, L. A. B., Bonomi, A. Technical and economic assessment of trash recovery in the sugarcane bioenergy production system. Scientia Agricola, 70 (5), 353-360, 2013.

Cavalett, O., Cunha, M.P., Chagas, M.F., Junqueira, T. L., Dias, M.O.S., Pavanello, L.G, Leal, M.R.L.V., Rossell, C.E.V, Bonomi, A. An exploratory economic analysis of sugarcane harvest extension using sweet sorghum in the Brazilian sugarcane industry. XXVIII ISSCT Congress, São Paulo, Brazil, 2013.

CEPEA - Center for Advanced Studies on Applied Economics (Centro de Estudos Avançados em Economia Aplicada). 2014. Available at: http://cepea.esalq.usp.br/english/. Accessed on August 20, 2014.

Ceres. “Ceres will launch new sorghum varieties in 2014/2015 season and celebrated performance in 2013/2014 season”(in Portuguese). September 15, 2014a. Available online at: http://www.ceres.net/ceressementes/Noticias/Releases/2014-15-09-Noticias.html.

Ceres. “Harvest extension”(in Portuguese). Accessed on October 6, 2014b. Available online at: http://www.ceres.net/ceressementes/Etanol/Etanol-Extender.html.

CHEN, J.C.P.; CHOU, C.C. Cane Sugar Handbook: A Manual for Cane Sugar Manufacturers and Their Chemists. Wiley and Sons, 12th ed., 1993, 1120 p.

CTBE – Brazilian Bioethanol Science and Technology Laboratory, 2012. The Virtual Sugarcane Biorefinery (VSB): 2011 Report. Available online at: www.bioetanol.org.br.

Cutz, L., Santana, D. Techno-economic analysis of integrating sweet sorghum into sugar mills: The Central American case. Biomass and Bioenergy, 68, 195-214, 2014.

Ferreira-Leitão, V.; Gottschalk, L. M. F.; Ferrara, M. A.; Nepomuceno, A. L.; Molinari, H. B. C.;Bon, E. P. S. Biomass residues in Brazil: availability and potential uses. Waste and Biomass Valorization, 1, 65-76, 2010.

Milanez, A. Y. et al. Ethanol production through integration of corn in the sugarcane mills: environamental and economic assessment and politic sugestions.(in portuguese) [A produção de etanol pela integração do milho-safrinha às usinas de cana-de-açúcar: avaliação ambiental, econômica e sugestões de política]. Revista do BNDES n.° 41, 2014.

MME – Ministry of Mines and Energy (Ministério de Minas e Energia). Available at: http://www.mme.gov.br/programas/leiloes_de_energia/menu/inicio.html. Accessed on August 20, 2014.

NOVACANA. “Sweet sorghum is alternative for sugarcane intercrop” (in portuguese). April 22, 2013. Available at: http://www.novacana.com/n/etanol/alternativas/sorgo-sacarino-alternativa-entressafra-cana-220413/.

Pacheco, T. F. “Tecnologia Industrial”, in May, A et al. (eds.) Sistema Embrapa de Produção Agroindustrial de Sorgo Sacarino para Bioetanol Sistema BRS1G – Tecnologia Qualidade Embrapa. Documentos 139 - Embrapa Milho e Sorgo. Sete Lagoas, MG, pp. 92-106, 2012.

Parrella, R.A.C and Schaffert, R.E.”Cultivares”, in May, A et al. (eds.) Sistema Embrapa de Produção Agroindustrial de Sorgo Sacarino para Bioetanol Sistema BRS1G – Tecnologia Qualidade Embrapa. Documentos 139 - Embrapa Milho e Sorgo. Sete Lagoas, MG, pp.14-22, 2012.

Pereira, L. G, Dias, M.O.S, Junqueira, T. L., Pavanello, L.G., Chagas, M.F., Cavalett, O., Maciel Filho, R., Bonomi, A. Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part II: Integration to a second generation sugarcane distillery. Chemical Engineering Research and Design, 92, 1452–1462, 2014.

Souza, E. L. L. and Macedo, I. C. (Coord.). Ethanol and Bioelectricity: Sugarcane in the Future of the Energy Matrix. São Paulo: Luc Projetos de Comunicação, 2010.

UDOP - Union of Bioenergy Producers (União dos Produtores de Bioenergia) Indicadores: Consecana. 2014. Available online at: www.udop.com.br. Accessed on August 2014.

7. Conclusions and suggestions for future work

7.1. Conclusions

Sugar energy-sector plays an important role in the Brazilian economy and the participation of its products, especially ethanol and electricity, on the energy matrix has increased in the last years.

It is well-known that the success of sugarcane-based ethanol production was motivated by its association to sugar production, which increased the Brazilian competitiveness in the international market for sugar and ethanol and reduced its susceptibility to market oscillations. Besides the synergies in the sugar and ethanol production processes that allow reducing costs, the sugarcane biorefineries can take advantage of their flexibility, diverting more sugars to ethanol or sugar production according to the market trends and business strategy aiming at the increase of profitability.

In this work, integration of sugar production in a first generation ethanol plant was evaluated, showing that production of sugar increases the profitability of the sugarcane biorefineries, taking into account the prices used in such evaluation. Moreover, an assessment of flexible annexed plants was performed considering the change of product mix according to monthly prices. Although the flexible configuration presents higher investment, its internal rate of return is higher than that of a unit diverting half of sugarcane juice for each product. The flexibility is even more important if sugar or ethanol prices increase.

In addition, electricity has been consolidated as a sugarcane biorefinery product due to the possibility of selling it to the grid. As a result, more efficient cogeneration systems – using high-pressure boilers (e.g., 65 bar) and extraction-condensing turbines – have been introduced in the sugar-energy sector, allowing the increase of electricity surplus (up to 92 kWh/t of sugarcane). The availability of straw, due to banishment of burning practices, has also contributed to larger generation of electricity. Considering that half of straw produced is used as fuel in the boiler, it is possible to double the electricity surplus. Compared to a scenario with a low efficiency cogeneration system and no use of straw, this scenario significantly improved the economic impacts (higher IRR and NPV).

Due to the large volume and high organic matter of vinasse, the valorization and proper destination of this effluent must be investigated. In this sense, vinasse biodigestion was evaluated considering two alternatives for biogas utilization: use as fuel in the cogeneration system and upgrade for use as natural gas replacement. The latter showed great potential, resulting in the highest IRR among the evaluated biorefinery scenarios. However, this alternative requires some incentives, since a connection to the grid is necessary in order to transport the upgraded biogas. It is worthwhile to mention that the drivers for implementation of vinasse biodigestion are not only economic, but mainly environmental, since there are still concerns on impacts of vinasse disposal. The introduction of second generation process will contribute to produce even larger quantities of vinasse, reinforcing the need for further research.

Product diversification, based on ethanol, sugar, electricity and biogas, demonstrated to be an important strategy towards the improvement of sugarcane biorefinery feasibility. The inclusion of other products in the biorefinery portfolio reduces ethanol production costs, increases profitability and improves business stability. Further studies have to be carried out for other products as higher alcohols or chemicals.

In addition, extension of operating period of sugarcane biorefineries was also evaluated. As a first approach, the year-round generation of electricity, using stored lignocellulosic material, increased the profitability of the plant without need for adaptation or other feedstock. This scenario was economically more attractive than the alternative based on juice storage for ethanol production in the off-season, which required more energy for concentration and also a higher investment.

The use of sweet sorghum as drop-in feedstock presented the best results, especially if the facility can operate during two months. This favorable result was achieved due to the increase of both ethanol and electricity production and because there is no need for additional investment. Although some sugarcane mills have used sweet sorghum for this purpose, there are still some challenges in order to be consolidated as a complementary feedstock.

The second generation process was also evaluated as an alternative for year-round operation. Considering some optimistic figures, the integrated 1G2G process presented a similar

IRR to the Base Case (1G plant operating only in the season) and a larger NPV, which indicate 2G is an attractive alternative, especially if the investment is reduced.

Regardless the alternative for extending operation period, a change in the sector paradigm is important, especially on efforts to reduce maintenance period. A better utilization of the infrastructure is essential to increase production, reduce costs and guarantee a regular supply all year-round. Besides, additional experiments with different feedstock must be carried out in order to have more information about the level of adequacy and yields in agricultural and industrial processes achieved for each feedstock.

In order to understand the impacts of enzymatic hydrolysis and enzyme features on 2G feasibility, a mathematical model was formulated. It was observed that enzyme price has a relevant influence on the definition of enzymatic hydrolysis conditions, on ethanol production and, consequently, on production cost.

Finally, this thesis showed potential applications of the Virtual Sugarcane Biorefinery (VSB) to evaluate – from a techno-economic perspective – mature technologies, alternative configurations as well as processes in development stage. The VSB results can be used to identify technological bottlenecks and to guide research aiming at the improvement of process feasibility.

7.2. Suggestions for future work

This thesis evaluated several alternative configurations and processes in a biorefinery context. Other opportunities for research are presented here as suggestions for further work:

- Detailing of biodigestion process and evaluation of other alternative uses for biogas, such as diesel replacement in agricultural machinery;
- Assessment of alternatives for reduction on vinasse volumes, such as recirculation, concentration and high alcoholic content fermentation, as well as formulation of biofertilizers;
- Optimization of water balance in first generation ethanol plants;

- Evaluation of the use of energy cane for increased electricity production and/or second generation ethanol production as well as a complementary feedstock in the sugarcane off-season;
- Comparative evaluation of pretreatment methods taking into account the performance on enzymatic hydrolysis and fermentation and the impacts in the overall process;
- Assessment of alternative process configurations for second generation process, e.g. simultaneous saccharification and fermentation and cell recycling;
- Further studies on electricity consumption on second generation process, including solids transportation into pretreatment vessels, agitation of hydrolysis reactors, etc;
- Inclusion of on-site enzyme production, considering inputs, energy consumption and equipment;
- Evaluation of water balance in the integrated first and second generation process, including reuse possibilities.
- Inclusion of other feedstocks for second generation ethanol production, such as forest residues and biomass sorghum;
- Inclusion of added-value products using pentoses as raw material;
- Assessment of a thermochemical route for production of ethanol and other biofuels;
- Inclusion of advanced cogeneration systems, such as biomass integrated gasification gas turbine (BIG-GT);

8. References

ADEN, A. et al. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*. Report No. NREL/TP-510-32438. Golden, CO: National Renewable Energy Laboratory, June 2002.

AGBOGBO, F. K. et al. Fermentation of glucose/xylose mixtures using Pichia stipitis. *Process Biochemistry*, v. 41, p. 2333–2336, 2006.

ALBARELLI, J. Q. *Produção de açúcar e etanol de primeira e segunda geração: simulação, integração energética e análise econômica*. PhD Thesis (Chemical Engineering), School of Chemical Engineering, University of Campinas, Campinas, 2013.

ALVES, M. *Estudo de sistemas de cogeração em usinas de açúcar e álcool, com utilização do bagaço e palha da cana*. Master's thesis (Chemical Engineering), School of Chemical Engineering, University of Campinas, Campinas, 2011.

ALVIRA, P. et al. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresour. Technol*., v. 101, p. 4851–4861, 2010.

ALZATE, C. A. C.; TORO, O. J. S. Energy consumption analysis of integrated flowsheets for production of fuel ethanol from lignocellulosic biomass. *Energy*, v. 31, p. 2447–2459, 2006.

ATALA, D. I. P. *Montagem, instrumentação, controle e desenvolvimento experimental de um processo fermentativo extrativo de produção de etanol*. PhD Thesis (Food Engineering), Faculty of Food Engineering, University of Campinas, Campinas, 2004.

BALAT, M. Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. *Energy Convers. Manage*., v. 52 (2), p. 858-875, 2011.

BARTA, Z. et al. Process design and economics of on-site cellulase production on various carbon sources in a softwood-based ethanol plant. *Enzyme Res.*, v. 2010, Article ID 734182, 8 pages, 2010.

BASTOS, V.D.. Etanol, alcoolquímica e biorrefinarias. *BNDES Setorial*, Rio de Janeiro, n. 25, p. 5-38, 2007.

BNDES; CGEE. *Sugarcane-Based Bioethanol: Energy for Sustainable Development*. Rio de Janeiro: BNDES, 2008.

CARDONA, C.A.; QUINTERO, J.A.; PAZ, I.C. Production of bioethanol from sugarcane bagasse: Status and perspectives. *Bioresour. Technol.*, v. 101, p. 4754-4766, 2010.

CAVALETT, O. et al. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. *Clean Technol. Environ. Policy*, v.14, p. 399-410, 2012.

CGEE. *Bioetanol combustível: uma oportunidade para o Brasil*. Brasília: CGEE, 2009.

CHANDEL, A. K. et al. Bioconversion of pentose sugars into ethanol: A review and future directions. *Biotechnol. Mol. Biol. Rev.*, v. 6 (1), p. 8-20, 2011.

CHAVEZ -RODRIGUEZ, M. F.; NEBRA, S. A. Assessing GHG Emissions, Ecological Footprint, and Water Linkage for Different Fuels. *Environ. Sci. Technol.*, v. 44, p. 9252–9257, 2010.

CHEN, J.C.P.; CHOU, C.C. *Cane Sugar Handbook: A Manual for Cane Sugar Manufacturers and Their Chemists*. Wiley and Sons, 12th ed., 1993, 1120 p.

CHERUBINI, F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manage.*, v. 51, p. 1412–1421, 2010.

CONAB. *Perspectivas para a agropecuária v.1-safra 2013/2014*, 2013. Available at: <http://www.conab.gov.br>. Accessed on September 2014.

CONAB. *Perfil do Setor do Açúcar e do Álcool no Brasil – safra 2011/2012*, 2013. Available online at: <http://www.conab.gov.br>. Accessed on August 2014.

CONAB. *Acompanhamento de safra brasileira Cana-de-açúcar, v. 1 – Safra 2014/15*. 2014. Available at: <http://www.conab.gov.br>. Accessed on January 2015.

COPERSUCAR. Processo de produção de High Test Molasses. *Cadernos Copersucar*. Série Industrial, n. 014. Piracicaba; 1985.

CORREIA NETO, J. F. *Elaboração e avaliação de projetos de investimento: considerando o risco*. Rio de Janeiro: Elsevier, 2009.

CTBE. *The Virtual Sugarcane Biorefinery (VSB): 2011 Report*, 2012. Available online at: http://ctbe.cnpem.br/pesquisa/avaliacao-integrada-biorefinarias/. Accessed on January 2015.

CUTZ, L.; SANTANA, D. Techno-economic analysis of integrating sweet sorghum into sugar mills: The Central American case. *Biomass Bioenergy*, v. 68, p. 195-214, 2014.

DEFILIPPI FILHO, L. C. *Estudo de viabilidade do uso do palhiço para geração de energia na entressafra de uma usina sucroenergética*. Master's thesis (Agroenergy), School of Economics São Paulo, Fundação Getúlio Vargas, São Paulo, 2013.

DIAS, M.O.S. *Desenvolvimento e otimização de processos de produção de etanol de primeira e segunda geração e eletricidade a partir da cana-de-açúcar*. PhD Thesis (Chemical Engineering), School of Chemical Engineering, University of Campinas, Campinas, 2011.

DIAS, M. O. S. et al. Simulation of integrated first and second generation bioethanol production from sugarcane: comparison between different biomass pretreatment methods. *J. Ind. Microbiol. Biotechnol*., v. 38, p. 955-966, 2011.

DIAS, M. O. S. et al. Improving second generation ethanol production through optimization of first generation production process from sugarcane. *Energy*, v. 43 (1), p. 246-252, 2012a.

DIAS, M. O. S. et al. Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash, *Bioresour. Technol.*, v. 103, p. 152-161, 2012b.

DIAS, M. O. S. et al. Improving bioethanol production – Comparison between extractive and low temperature fermentation. *Appl. Energy*, v. 98, p. 548–555, 2012c.

DIAS, M. O. S. et al. Cogeneration in integrated first and second generation ethanol from sugarcane. *Chem. Eng. Res. Des.,* v. 91, p. 1411-1417, 2013.

DIAS, M. O. S. et al. Butanol production in a sugarcane biorefinery using ethanol as feedstock - Part I: integration to a first generation sugarcane distillery. *Chem. Eng. Res. Des.,* v. 92, p. 1441-1451, 2014.

DURÃES, F.O.M. "Sorgo sacarino: desenvolvimento de tecnologia agronômica". In: *Agroenergia em Revista*, Ano II, ed nº 3, p.7, 2011.

ENSINAS, A.V.; ARNAO, J.H.S; NEBRA, S.A. "Increasing energetic efficiency in sugar, ethanol, and electricity producing plants". In: CORTEZ, L. A. B. (Coord.). *Sugarcane bioethanol — R&D for Productivity and Sustainability*, São Paulo: Editora Edgard Blücher, p.583-600, 2014.

EPE. *Análise de Conjuntura dos Biocombustíveis - Ano 2013*, 2014. Available at: <http://www.epe.gov.br/>. Accessed on November, 2014.

EPE. *National Energy Balance 2013 – 2012 Base Year: Final Report*, 2013. Available at: <http://www.mme.gov.br/>. Accessed on May 2014.

FATOR BRASIL. *Usina da Pedra processa 13 mil toneladas de palhada da cana-de-açúcar para cogeração de energia*. August 2013. Available at: <http://www.revistafatorbrasil.com.br/ver_noticia.php?not=245020>. Accessed on April 2014.

FERNANDES, S. *Mistura de etanol na gasolina deve subir de 25 % para 27 % neste mês*. In: Folha de S. Paulo. February 2015. Available at: <http://www1.folha.uol.com.br/ mercado/2015/02/1583981-governo-eleva-mistura-de-etanol-na-gasolina-para-27.shtml>. Accessed on February 2015.

FERREIRA-LEITÃO, V. et al. Biomass residues in Brazil: availability and potential uses. *Waste and Biomass Valorization*, v. 1, p. 65-76, 2010.

FU, N.; PEIRIS, P.; MARKHAM, J.; BAVOR, J. A novel co-culture process with Zymomonas mobilis and Pichia stipitis for efficient ethanol production on glucose/xylose mixtures. *Enzyme Microb. Technol.*, v. 45, p. 210–217, 2009.

GALBE, M.; ZACCHI, G. Pretreatment of lignocellulosic materials for efficient bioethanol production. *Adv. Biochem. Eng.Biotechnol.*, v. 108, p. 41–65, 2007.

GÍRIO, F. M. et al. Hemicelluloses for fuel ethanol: A review. *Bioresour. Technol.*, v. 101, p. 4775-4800, 2010.

GRANBIO, 2014. GranBio begins producing second-generation ethanol. Available online at: <http://www.granbio.com.br>. Accessed on January 2015.

HASSUANI, S.J.; LEAL M.R.L.V.; MACEDO I.C. (eds). *Biomass Power Generation—Sugarcane Bagasse and Trash*. CTC and PNUD, Piracicaba, 2005.

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.* Available online at: <http://www.nrel.gov>. Accessed on May 2012.

IEA BIOENERGY. *Biogas Upgrading and Utilisation, Task 24- Energy from biological conversion of organic waste*, 2001. Available at: <http://www.biogasmax.eu>. Accessed on November 2014.

IEA. *Technology Roadmap: Bioenergy for Heat and Power*, 2012. Available at: <http://www.iea.org>. Accessed on November 2014.

IEA. *Technology Roadmaps: Biofuels for Transport*, 2011. Available at: <http://www.iea.org>. Accessed on November 2014.

INFORMA ECONOMICS FNP. *Usina pioneira de etanol de milho consolida a produção em escala comercial em Mato Grosso*, 2013. Available at: <http://www.informaecon-fnp.com/noticia/9530>. Accessed on July 2014.

JUNQUEIRA, T.L. *Simulação de colunas de destilação convencional, extrativa e azeotrópica no processo de produção de bioetanol através da modelagem de não equilíbrio e da modelagem de estágios de equilíbrio com eficiência*. Master's thesis (Chemical Engineering), School of Chemical Engineering, University of Campinas, Campinas, 2010.

KARP, S.G. et al. Pretreatment strategies for delignification of sugarcane bagasse: a review. *Braz. Arch. Biol. Techn.*, v.56, 4, p. 679-689, 2013.

KLEIN-MARCUSCHAMER, D. et al. The Challenge of Enzyme Cost in the Production of Lignocellulosic Biofuels. *Biotechnol Bioeng*, v. 109, p.1083-1087, 2012.

KUMAR, P. et al. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind. Eng. Chem. Res.*, v. 48, p. 3713-3729, 2009.

LIN, Y.; TANAKA, S. Ethanol fermentation from biomass resources: current state and Prospects. *Appl. Microbiol. Biotechnol.*, v. 69, p. 627-642, 2006.

MACEDO, I.C.; SEABRA, J.E.A.; SILVA, J.E.A.R. 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*, v. 32 (7), p. 582-595, 2008.

MACRELLI, S. *Ethanol from sugarcane lignocellulosic residues - Opportunities for process improvement and production cost reduction*. PhD Thesis (Engineering), Department of Chemical Engineering, Lund University, Sweden, 2014.

MACRELLI, S.; MOGENSEN, J.; ZACCHI, G. Techno-economic evaluation of 2nd generation bioethanol production from sugar cane bagasse and leaves integrated with the sugar-based ethanol process. *Biotechnol. Biofuels*, 5:22, 2012.

MANTELATTO, P. E. *Estudo do processo de cristalização de soluções impuras de sacarose por resfriamento*. Master's thesis (Chemical Engineering), School of Chemical Engineering. Federal University of São Carlos, São Carlos, 2005.

MAPA. *2012: statistical yearbook of agrienergy*, 2013. Available at: <http://www.agricultura.gov.br/>. Accessed on May 2014.

MAPA. *Produção Brasileira de Cana-de-açúcar, Açúcar e Etanol. Setor Sucroalcooleiro 20.02.2015.* Available at: http://www.agricultura.gov.br/. Accessed on February 2015.

MARIANO, A.P. et al. Butanol production in a first-generation Brazilian sugarcane biorefinery: Technical aspects and economics of greenfield projects. *Bioresour. Technol*., v. 135, p. 316-323, 2013a.

MARIANO, A.P. et al. Utilization of pentoses from sugarcane biomass: Techno-economics of biogas vs. butanol production. *Bioresour. Technol*., v. 142, 390-399, 2013b.

MARTÍN, C.; E THOMSEN, A. B. Wet oxidation pretreatment of lignocellulosic residues of sugarcane, rice, cassava and peanuts for ethanol production. *J. Chem. Technol. Biotechnol*., v. 82, 174-181, 2007.

MARTÍN, C.; KLINKE, H. B.; THOMSEN, A. B. Wet oxidation as a pretreatment method for enhancing the enzymatic convertibility of sugarcane bagasse. *Enzyme Microb. Technol.*, v. 40, p. 426-432, 2007.

MATSUOKA, S. et al. Energy cane: its concept, development, characteristics, and prospects. *Adv. Bot.*, v. 2014, article ID 597275, 13 pages, 2014.

MEYER, J. et al. *Good management practices manual for the cane sugar industry*. International Finance Corporation, São Paulo, Brazil, 2011.

MILANEZ, A. Y. et al. A produção de etanol pela integração do milho-safrinha às usinas de cana-de-açúcar: avaliação ambiental, econômica e sugestões de política. *Revista do BNDES*, n. 41, 2014.

MORAES, B. S. et al. Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? *Appl. Energy*, v. 113, p. 825–835, 2014.

MORAES, B.S; ZAIAT, M.; BONOMI, A. Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: Challenges and perspectives. *Renew. Sust. Energ. Rev.*, v. 44, p. 888–903, 2015.

MOSIER, N. et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.*, v. 96, p. 673-686, 2005.

MURPHY, J. D.; POWER, N. M. An argument for using biomethane generated from grass as a biofuel in Ireland. *Biomass Bioenergy*, v. 33, p. 504 – 512, 2009.

MUSSATTO, S. I. et al. Technological trends, global market, and challenges of bio-ethanol production. *Biotechnol. Adv.*, v. 28, p. 817-830, 2010.

NOVACANA. Sorgo sacarino é alternativa na entressafra de cana. April 2013. Available at: <http://www.novacana.com/n/etanol/alternativas/sorgo-sacarino-alternativa-entressafra-cana-220413/>. Accessed on July 2013.

OLIVERIO J. L. et al. Juice Extraction Systems: Mills and Diffusers – The Brazilian Experience, *Proceeding of XXVIII International Society of Sugar Cane Technologists Congress*, 2013.

PACHECO, T. F. “Tecnologia Industrial”. In: MAY, A. et al. (eds.) *Sistema Embrapa de Produção Agroindustrial de Sorgo Sacarino para Bioetanol Sistema BRS1G – Tecnologia Qualidade Embrapa. Documentos 139.* Embrapa Milho e Sorgo, Sete Lagoas, MG, p. 92-106, 2012.

PALACIOS-BERECHE, R. *Modelagem e integração energética do proceso de produção de etanol a partir da biomassa de cana-de-açúcar*. PhD Thesis (Mechanical Engineering), School of Mechanical Engineering, University of Campinas, Campinas, 2011.

PANDEY, A. et al. Biotechnological potential of agro-industrial residues. I: sugarcane bagasse. *Bioresour. Technol*,.v. 74, p. 69-80, 2000.

PARRELLA, R.A.C; SCHAFFERT, R.E."Cultivares". In: MAY, A. et al. (eds.) *Sistema Embrapa de Produção Agroindustrial de Sorgo Sacarino para Bioetanol Sistema BRS1G – Tecnologia Qualidade Embrapa. Documentos 139*. Embrapa Milho e Sorgo, Sete Lagoas, MG, p.14-22, 2012.

PEREIRA, L. G. et al. Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part II: Integration to a second generation sugarcane distillery. *Chem. Eng. Res. Des.*, v. 92, p. 1452–1462, 2014.

PORTO, G., 2011. Usina produz pela primeira vez etanol a partir de sorgo. In: *O Estado de S. Paulo.* Available at: http://economia.estadao.com.br/noticias/geral,usina-produz-pela-primeira-vez-etanol-a-partir-de-sorgo-imp-,705475. Accessed on May 2013.

RABELO, S. C. *Avaliação e otimização de pré-tratamentos e hidrólise enzimática do bagaço de cana-de-açúcar para a produção de etanol de segunda geração*. PhD Thesis (Chemical Engineering), School of Chemical Engineering, University of Campinas, Campinas, 2010.

RAÍZEN, 2015. *Tecnologia em energia renovável – Etanol de segunda geração*. Available at: <http://www.raizen.com.br/energia-do-futuro-tecnologia-em-energia-renovavel/etanol-de-segunda-geracao>. Accessed on January 2015.

RIVERA, E. C. et al. Enzymatic hydrolysis of sugarcane bagasse for bioethanol production: Determining optimal enzyme loading using neural networks. *J. Chem. Technol. Biotechnol.*, v. 85, p. 983-992, 2010.

SALOMON, K. R.; LORA, E. E. S. Estimate of the electric energy generating potential for different sources of biogas in Brazil. *Biomass Bionergy*, v. 33, p. 1101-1107, 2009.

SANTOS, F. A. *Análise da aplicação da biomassa da cana como fonte de energia elétrica: usina de açúcar, etanol e bioeletricidade*. Master's thesis (Engineering), Polytechnic School of the University of São Paulo, São Paulo, 2012.

SCANDIFFIO, M. I. G. *Análise prospectiva do álcool combustível no Brasil – cenários 2004-2024*. PhD Thesis (Mechanical Engineering), School of Mechanical Engineering, University of Campinas, Campinas, 2005.

SEABRA, J. E. A. et al. A techno-economic evaluation of the effects of centralized cellulosic ethanol and co-products refinery options with sugarcane mill clustering. *Biomass Bioenergy*, v. 34, p. 1065-1078, 2010.

SERMATEC, 2015. *Etanol*. Available at: < http://media.sermatec.com.br/uploads /produtos_arquivo/1_catalogo_sermateczanini_etanol_3.pdf>. Accessed on February 2015.

SILVA, A. S. et al. "Sugarcane and Woody Biomass Pretreatments for Ethanol Production". In: CHANDEL, A.; SILVA, S. S. (Eds.), *Sustainable Degradation of Lignocellulosic Biomass - Techniques, Applications and Commercialization*. InTech, 2013.

SORDI, R. A. "Sorgo sacarino para produção de etanol: uma visão do produtor e da usina de cana-de-açúcar". In: *Agroenergia em Revista*, Ano II, ed nº 3, p.31-32, 2011.

SUN, Y.; CHENG, J. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresour. Technol*., v. 83, p. 1-11, 2002.

SWAYZE, S. The sweet sorghum opportunity: A complementary source of low-cost fermentable sugars for biofuels. *Int. Sugar J.*, v.111 : 1331, p. 691-695, 2009.

VEJA, 2015. *Em seis anos, 83 usinas de cana encerraram atividades.* Available at: http://veja.abril.com.br/noticia/economia/em-seis-anos-83-usinas-de-cana-encerraram-atividades/. Accessed on February 2015.

WALTER, A.; DOLZAN, P. *Country Report 2011: Brazil – Task 40 – Sustainable Bio-energy Trade; securing Supply and Demand*, 2012. Available at: <http://www.bioenergytrade.org/>. Accessed on October 2014.

WILKIE A.C.; RIEDESEL K.J.; OWENS J.M. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. *Biomass Bioenergy*, v. 19, p. 63-102, 2000.

YANG, B. E; WYMAN, C. E. Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels Bioprod. Bioref.*, v. 2, p. 26-40, 2008.

ZALDIVAR, J.; NIELSEN, J.; OLSSON, L. Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration. *Appl. Microbiol. Biotechnol.*, v. 56, p. 17–34, 2001.

ZHANG, X. et al. Ethanolic cofermentation with glucose and xylose by the recombinant industrial strain Saccharomyces cerevisiae NAN-127 and the effect of furfural on xylitol production. *Bioresour. Technol.*, v. 101, p. 7093–7099, 2010.