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Sugarcane processing for ethanol and sugar in Brazil



DEVELOPMENT

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ABSTRACT

Sugarcane has been used as feedstock for production of ethanol on a large scale basis in Brazil for over three decades, where most of the sugarcane mills produce sugar, ethanol and electricity. In this study the technologies usually employed in sugarcane mills in Brazil are briefly described, along with opportunities for process improvements and suggestions for the future of the sugarcane industry. These technologies and improvements can be improved, adapted and replicated to other countries using new technologies and alternative feedstock throughout the world.

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1. Introduction

Brazil is a traditional sugar producer since the beginning of the XVII century, and ethanol started to become an important product for transport sector in the early XX Century, using molasses from sugar production as feedstock. The presently prevailing production model where ethanol and sugar are

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produced in an integrated process became important after the launch of the Brazilian Alcohol Program (Proalcool) in 1975, when the urgent necessity of expanding ethanol production was met mainly by annexing distilleries to existing sugar mills (Soccol et al., 2010). After the second oil shock in 1979, the government decided to increase even further ethanol production, thus autonomous distilleries were deployed. However, with the sharp fall of oil prices in 1986 and the consequent decrease of government interest on the ethanol program, the production stagnated. In 1990 the government began to deregulate the sector and sugar exports were liberated, so Brazil became a very competitive sugar producer: exports increased from around one million tonnes in 1991 to 19 million tonnes in 2007 (MAPA, 2014). As a consequence, sugar factories were installed annexed to existing autonomous distilleries, consolidating once again the prevailing model of producing sugar and ethanol in an integrated way. Nevertheless, in the recent new expansion phase that started in 2004, several autonomous distilleries were built to attend the expected future demand of ethanol, both domestic (mostly driven by the flex fuels engines) and international (mostly driven by the need of renewable fuels to attend mandates of target reduction of greenhouse gases emissions in several countries).

The sector is currently in a transition from processing burned whole cane to unburned (green) chopped cane due to the gradual phase out of sugarcane burning (Alonso Pippo et al., 2011). Even though the government established a longer time frame for phase out of sugarcane burning, due to environmental and economic reasons, the sector itself decided to reduce that time frame and totally extinguish sugarcane burning (in mechanized areas, where soil declivity is lower than 12%) by 2014. Thus, manual harvest has been increasingly replaced by mechanized unburned harvest (Galdos et al., 2013). Therefore, the sector has been facing changes in the sugarcane quality (mainly increased external matter content), with consequent impacts on cane processing and on soil characteristics.

In this work, the prevailing sugarcane processing technologies and the corresponding improved technologies, using the most common processing model (combined ethanol and sugar production) as reference are briefly described. After that, some critical opportunities for process improvements and some suggestions for the sustainable future of sugarcane industry in Brazil are proposed.

2. Sugarcane processing

In a typical sugarcane mill, the stages illustrated in Fig. 1 are present.

The typical mill has an upfront section that is common to the ethanol distillery and sugar factory composed by the following processes: cane reception, cane preparation and juice extraction. The extracted juice is sent to the juice treatment system, in which impurities are removed from the juice in order to provide an adequate material for the subsequent steps; although most of the operations of juice treatment are common for both sugar and ethanol production, each process has its own specificities. During processing in the sugar factory, a concentrated residual solution obtained after sugar crystallization (molasses) is produced. Sugarcane juice from the ethanol juice treatment is blended with molasses, fermented using yeast (which is recovered and reused in the fermentation process), and the fermentation product containing ethanol is sent for distillation and dehydration. In the sugar house the juice is concentrated, crystallized, centrifuged and dried.

All the energy (steam and electricity) needed in this process is produced by the mill using sugarcane bagasse as fuel. In many mills surplus power is generated for sale to the grid. Some mills have been recovering a fraction of the sugarcane straw (sugarcane tops and leaves) and using it as fuel as well, however this is not yet a common practice in Brazilian facilities due to high recovery costs and questions about short and long term soil implications (Cardoso et al., 2013). However, sugarcane burning phase out provides an opportunity for straw use.

In Sections 2.1–2.3 the prevailing process technologies are briefly described.

2.1. Shared operations

2.1.1. Cane reception

Upon arrival at the factory, mechanically harvested sugarcane is discharged upon tables and sent to the cleaning system or directly to the feeding tables that lead to the cane preparation section. In the



Fig. 1. Simplified scheme of first generation sugar and ethanol production from sugarcane.

case of chopped sugarcane, a dry cleaning system should be used in order to prevent sugar losses. In this stage some mineral and vegetable impurities are removed and cleaned cane is sent to cane preparation.

2.1.2. Cane preparation

Sugarcane is chopped in a series of knives and shredders which promote cell opening and lead to a uniform cane layer, producing an adequate material for the subsequent step (juice extraction). Previously to extraction, a magnet is used for metal removal.

2.1.3. Extraction of sugars

Juice extraction in Brazil is mainly carried out using mills, which consist of sets of three to five rolls where sugarcane is pressed, separating juice from bagasse (fibrous fraction of the sugarcane stalks). Usually groups of four to six mills in tandem (sets of rolls) are employed, with bagasse from the first mill being fed to the subsequent mill and so forth; warm water for imbibition is added in the last tandem, increasing sugar recovery in the juice. Juice produced in the last tandem is used as imbibition to increase the extraction of sugars in the previous tandem, and so forth up to the third mill tandem. Sugarcane juice is sent to a screen, where a fraction of the fibers dragged with the juice are removed and recycled to the second mill for recovery of sugars. Usually, juice from the first mill is sent to sugar production because it contains higher sugar purity, while juice obtained in the second mill (called mixed juice) is diverted for ethanol production.

Mills and other equipment in the cane preparation are usually driven by steam turbines, which require more energy as steam than electric energy in efficient electric engines.

Diffusers can also be used in juice extraction with increased sugar recovery and less energy consumption than the milling tandem (Palacios-Bereche et al., 2014a).

2.1.4. Cogeneration systems

Sugarcane facilities currently use a cogeneration system based on the Rankine cycle, in which sugarcane bagasse is burnt in the boiler, producing steam that is expanded in turbines coupled with electric generators; turbines exhaust steam is used as thermal energy source for the various unit operations of the sugar and ethanol production process. Most facilities use only back-pressure steam turbines, which limit the amount of fuel that can be burnt to supply the steam demand of the process (Serra et al., 2009).

Up until the late 1990s, cogeneration systems employed in the mills have been designed only to meet the thermal energy needs of the sugar and ethanol production process, burning all the bagasse available and producing little or no surplus electricity. De-regulation of the power sector in Brazil in the 1990s created conditions for the mills and other electricity producers to sell their electricity to the grid, promoting a modernization of existing cogeneration facilities (Leal et al., 2013). Modern mills have replaced low pressure/low efficiency boilers by medium and high pressure boilers (42–90 bar) (Seabra and Macedo, 2011). Systems with condensing–extraction steam turbines allow the maximization of electricity production, since the amount of steam produced does not have to match the one required to supply thermal energy for the process, as excess steam can be condensed (Dias et al., 2011a).

2.2. Ethanol production

2.2.1. Juice treatment

As mentioned before, sugarcane juice obtained at the second milling tandem is sent to ethanol production. Juice produced in the mills contains several impurities (minerals, salts, organic acids, dirt and fine fiber particles), which must be removed prior to fermentation. Juice treatment is comprised by a physicochemical treatment consisting of separation of fibers and sand in screens, heating of juice from 30 to 70 °C, addition of lime along with a second heating, up to 105 °C, removal of air (flash) and addition of a flocculant polymer and final removal of impurities through a clarification process. Mud obtained in the clarifier is filtrated to improve sugars recovery, as illustrated in Fig. 2.

Even though features illustrated in Fig. 2 represent the desirable characteristics of juice treatment for ethanol production in order to promote an adequate pH and impurities content for fermentation, differences may be found among existing mills.



Fig. 2. Simplified scheme of the juice treatment process for ethanol production.

2.2.2. Juice concentration

Clarified juice must be concentrated to achieve an adequate sugar concentration for fermentation. In ethanol production, when mixing molasses from the sugar factory cannot achieve the required sugar concentration, standard evaporators are usually employed, although multiple effect evaporators have lower steam consumption (Dias et al., 2012a). In juice evaporation, steam obtained as a purge or bleed (vegetal vapor) is used as utility in the process.

2.2.3. Fermentation

Conversion of sugars into ethanol usually takes place in a fed-batch fermentation process with cells recycle; in this process configuration, yeast (*Saccharomyces cerevisiae*) recovered from a previous fermentation batch is fed to the fermentor prior to the juice; after addition of the juice, the mixture remains in the reactor for a few hours, and the sugars are fermented into ethanol and by-products (other alcohols, organic acids, etc.), simultaneously producing carbon dioxide. The process takes place at temperatures around 30–34 °C and produces wine with relatively low ethanol content (up to 10 °GL) due to yeast inhibition related to substrate, product and temperature. Fermentation vats are usually closed and carbon dioxide recovered is washed in absorption columns in order to recover carried over ethanol, which is sent to distillation. The fermented liquor (wine) produced in the fermentation is centrifuged to remove yeast cells, which undergo a chemical treatment using water and sulfuric acid to reduce bacterial contamination. Yeast cells are used on the next batch, while centrifuged wine is sent to distillation.

An alternative to this process is the continuous fermentation, which can be found in some mills and is based on the use of 3–5 reactors in series, using the same system for cells recycle described above.

2.2.4. Distillation

In order to produce fuel ethanol, wine must be purified to at least 95 °GL; centrifuged wine is purified in the distillation and rectification columns, producing hydrous (around 93 wt%) ethanol.

In Brazil, the most common configuration of the distillation columns is illustrated in Fig. 3. Wine is fed at the top of column A1, located between columns D and A. At the top of column D, volatile compounds are removed, while vinasse which contains mostly water is obtained at the bottom of column A. Ethanol-rich streams (phlegms) containing around 50 wt% ethanol are obtained at columns D and A. This first set of columns is called distillation. The second set, comprised by columns B and B1, is named rectification. Phlegms are fed to these columns, and the rest of the water is removed at the bottom of column B1, while hydrated ethanol is produced at the top of column B.



Fig. 3. Simplified scheme of the distillation process for production of hydrated ethanol (Bonomi et al., 2012).

Vinasse is used to pre-heat wine in the heat exchanger K. Wine is also pre-heated by heat exchange with ethanol vapor from the top of column B (E condenser) before it is fed into column A1. Vinasse is used in fertirrigation of the sugarcane fields, promoting nutrients (mostly potassium) recycle. Fusel oil, a mixture of organic compounds which has isoamyl-alcohol as its main component, is produced as a side stream of columns B–B1.

This configuration of the distillation columns presents relatively high steam consumption. Multiple effect operation of the distillation columns (Dias et al., 2012a) and production of wine of higher ethanol content (Dias et al., 2012b) are some options to reduce steam consumption in distillation.

2.2.5. Ethanol dehydration

In order to be used in a mixture with gasoline in gasoline-driven engines, ethanol must be concentrated to 99.3 wt%, at least. This purity must be accomplished by means of alternative purification systems, since ethanol and water form an azeotrope with ethanol concentration of around 95 wt%. The most common dehydration systems used in Brazil are azeotropic distillation with cyclohexane, extractive distillation with monoethyleneglycol and adsorption on molecular sieves.

2.2.5.1. Heterogeneous azeotropic distillation with cyclohexane. In this process cyclohexane is added to an azeotropic column, along with hydrated ethanol, and it forms a new tertiary heterogeneous azeotrope with ethanol and water. The azeotrope is removed at the top of the azeotropic column, while anhydrous ethanol is produced at the bottom. The ternary azeotrope is cooled and undergoes a liquid-liquid separation; the organic phase (rich in cyclohexane) is recycled to the azeotropic column, while the aqueous phase is sent to a recovery column where a solution containing ethanol is produced and recycled to the azeotropic column (Junqueira et al., 2009).

This process, in spite of its high energy consumption (Cavalett et al., 2012), remains the most common configuration used in sugarcane mills. Up until the late 1990s azeotropic distillation was the only alternative for production of anhydrous ethanol in Brazil, but benzene was the separation agent used until 1997, when its use was prohibited due to safety issues. Cyclohexane is therefore used in replacement of benzene, allowing the use of existing infrastructure.

2.2.5.2. Extractive distillation with monoethyleneglycol (MEG). Extractive distillation, also called homogeneous azeotropic distillation, consists of the addition of a third component (MEG) which alters the relative volatility of ethanol and water, promoting separation of anhydrous ethanol in an extractive column. In this case the solvent-water mixture is obtained at the bottom of the column, being fed to a second column which promotes solvent recovery. Anhydrous ethanol is obtained at the top of the extractive column.

This process was first introduced in industrial mills in Brazil in 2001. It presents relatively lower energy consumption and less contamination of the product with the separating agent than the heterogeneous azeotropic distillation.

2.2.5.3. Adsorption on molecular sieves. In contrast with the already mentioned dehydration processes based on distillation principles, in the adsorption no chemical solvent is used, but a zeolite bed is responsible for removal of water from the hydrated ethanol. In this process hydrated ethanol vapor is fed to the zeolite beds; three beds are usually used, in which one is regenerating and the other two are removing water, in a cyclic operation. When hydrated ethanol contacts the zeolites, water molecules are adsorbed while anhydrous ethanol is obtained at the bottom of the bed. During regeneration, water is removed from the zeolites by applying low pressure to the bed (Pressure Swing Adsorption), and the recovered water–ethanol mixture is recycled to the distillation columns.

This process has the lowest energy consumption among the industrial alternatives in Brazil, and has the advantage of producing ethanol with no solvent contamination.

2.3. Sugar factory

Sugarcane juice obtained at the first mill after screening is sent to sugar production, where it is purified and concentrated.

2.3.1. Juice treatment

Juice treatment for sugar production is ideally comprised by the same steps as the juice treatment for ethanol production for production of raw sugar (VHP – very high polarization, or VVHP – very very high polarization). However, more CaO is necessary for sugar production in comparison with ethanol. In the production of white sugar, SO_2 must be added in order to decrease the color of the syrup in a process called sulphitation.

2.3.2. Juice concentration

Clarified juice is concentrated in multiple effect evaporators, usually consisting of Robert evaporators with 4 or 5 evaporation steps, from around 15 °Brix (soluble solids content) to 65 °Brix. Vapors are extracted from the first and second effects and used as thermal energy source in operations involving heat on juice treatment, sugar production and distillation columns.

2.3.3. Boiling, crystallization and centrifuging

Different types of sugar can be produced: export (VHP or VVHP) and white sugar, for the domestic market; the main difference between them is the chemical treatment, which includes sulphitation in the white sugar production.

Prior to sucrose crystallization, water from the syrup is removed using vacuum pans, similarly to evaporators; inside the pans a mixture of sugar crystals and syrup, or mother liquor (the liquid fraction), is formed, named massecuite. After a certain residence time the massecuite is transferred to the crystallizers, which normally consist of mixing tanks with cooling system where sucrose is allowed to crystallize before centrifuging. The massecuite in the crystallizers is sent to centrifuges to separate crystal from run-off syrup (mother liquor), in which hot water and steam are used to wash the crystals.

Most sugar factories in Brazil use two-boiling systems, since it is not necessary to completely exhaust molasses, considering that molasses will be used as feedstock for fermentation (Chandel et al., 2014). The syrup obtained previously is conveyed to the subsequent crystallization step, which is carried out in vacuum evaporator crystallizers (batch or continuous) in two or three massecuites. In the two-boiling system, two types of sugars are produced. In the first centrifuge A-massecuite (produced in the first vacuum pancrystallizer sequence) is fed, sugar crystals are washed with water (and/or steam) and the run-off syrup (mother liquor) is drained, producing grade A sugar and A-molasses. These A-molasses are sent to pan B, where A-molasses are concentrated by evaporation and crystallization is initiated by seeding, consisting of the introduction of fine sucrose crystals. After an appropriate residence time, which depends on the type of equipment and agitation used, the B-massecuite is sent to the crystallizer, which includes a cooling system where further crystallization takes place and the mixture is stored prior to being centrifuged. Afterwards, B-massecuite is centrifuged in continuous basket centrifuges generating grade B sugar (magma) and molasses, which are sent to alcoholic fermentation. This grade B sugar is an intermediate sugar stream that is recycled and used as seed for the crystallization of A-massecuite in pan A. The A-massecuite is sent to the crystallizer, promoting further crystallization, and then it is feed in the basket centrifuge, producing A-sugar and A-molasses. The grade A sugar produced is either white sugar or raw sugar, depending on prior process characteristics.

2.3.4. Sugar drying

Sugar produced in the centrifuges is usually dried in a rotary drum drier, in which its moisture is reduced to around 0.05–2.0% depending on the type of sugar produced, then cooled and stored prior to distribution.

3. Sectorial process efficiencies and potential improvements

3.1. Reduction of energy consumption

With the possibility of selling surplus electricity to the grid, sugarcane mills have been improving the performance of their units to promote a reduction in the energy consumption in the process, as well as the production of higher amounts of electricity.

The use of electric drives for sugarcane preparation and extraction has been preferred lately over steam turbines, which are less efficient and require more steam. The use of diffusers instead of mills also allows decrease of steam consumption, since the amount of mechanical energy required to operate diffusers is significantly smaller than the energy required for mills (about 10 kWh/t of cane for diffusers compared to 15 kWh/t of cane for mills, according to Pellegrini and Oliveira Júnior (2011)). However, one or two additional mills are required to dry final bagasse.

Alternative fermentation processes such as low temperature or extractive fermentation allow production of wine with higher ethanol content leading to lower energy consumption in distillation (Dias et al., 2012b). Product recovery through the use of membranes can also be used to produce high ethanol concentration wines, but technological issues, such as membrane fouling remain to be solved (Abels et al., 2013).

Pinch Analysis has also been considered for the reduction of process steam consumption in sugarcane facilities. This analysis, based on thermal integration between hot and cold streams of the process, can significantly improve energy savings of conventional and future biorefinery configurations (Dias et al., 2011a; Palacios-Bereche et al., 2014b).

3.2. Reduction of water consumption

Another important integration issue that must be addressed is the use of water in the sugarcane mill. Bearing in mind that water resources are scarce, and that the sugarcane plant itself has around 70% of water, the need to reduce water consumption in sugarcane processing and to partially recover the water from the sugarcane plant has been increasingly addressed (Chavez-Rodriguez et al., 2013).

Thermal integration of the process through Pinch Analysis can promote a reduction of water consumption as well, since water is used as cold utility for the process (Albarelli et al., 2014). Large amounts of cold water are used in direct condensers and heat exchangers, being usually cooled using cooling towers. The substitution of direct contact condensers by high efficiency indirect condensers, along with thermal integration, decrease the amount of water used in the process, simultaneously reducing water losses through evaporation in cooling towers and water uptake. An efficient process could even produce water as a co-product – in fact, the possibility to export water from the sugarcane mill is a commercial technology, the process called Dedini Sustainable Mill (Olivério et al., 2010) in which the sugarcane processing facility allows the production of around 3.6 liters of water/liter of bioethanol. Some of the process improvements that can lead to significant reduction of water consumption are: recovery of condensates and use as imbibition water; multiple-effect juice evaporation and vinasse concentration with vapor bleeding for heating operations; and production of a fermented wine with the highest possible ethanol content. Some mills have already been using part of these technologies, reducing water withdrawal from around 1.0 to 0.3 m³ per ton of sugarcane.

3.3. Decreasing sugar losses

A major aspect of improving sugarcane processing consists of reduction of sugar losses. In fact, losses reduction could stimulate the competitiveness of the process, through a more efficient use of the feedstock that is already available at plant site. Among the total sugar losses in the conventional process, fermentation represents the most important source, as shown in Table 1.

Bearing this in mind, several technological alternatives have been proposed for the medium-long term in order to overcome these drawbacks and optimize ethanol production, adding value and improving the sustainability of the process. Such alternatives are expected to be implemented on industrial level in 5–15 years, depending on the capital and return on investment (ROI) required.

Sugarcane cleaning system with water has been gradually replaced by a dry cleaning system, since most of the sugar losses in this stage are due to the use of water. In addition, the possibility to recover the straw collected from the field along with sugarcane stalks motivates the use of a dry cleaning system, so that this lignocellulosic fraction can be used as fuel or even as feedstock for second generation ethanol production in the near future.

Value (%)	Contribution (%)
0.47	3.32
3.73	26.38
0.54	3.82
5.17	36.57
0.18	1.27
4.05	28.64
14.14	100.00
	Value (%) 0.47 3.73 0.54 5.17 0.18 4.05 14.14

 Table 1

 Sugar losses in the ethanol production process from sugarcane (CGEE, 2009).

Substantial changes in the fermentation process must be carried out in order to increase the efficiency of sugars use in this stage, but the main characteristics of the process (i.e., no significant changes are done to the configuration of the process, fed-batch or continuous with cells recycle) must be maintained. These changes are related to the increase of fermentation yield from the current average value of 89–91.5%, which could be accomplished by both "in situ" and "upstream" modifications of the process These changes include improvements on juice treatment, such as juice sanitization and in the near future sterilization, which could decrease sugar losses from bacterial contamination; chilling of fermentation vats, diminishing fermentation temperature from the current 34–35 °C to temperatures as low as 30 °C, what decreases inhibitory effects – this could be achieved by using chillers which could employ vinasse or low grade steam (bleeding vapor) as heat source; increase of ethanol content of the wine (up to 14 °GL) could also decrease vinasse volume and, therefore, ethanol losses in this stream; use of different yeast strains and an improved yeast cell treatment, which could enhance process stability; improve the automation of the process, using sensors and increasing process control.

3.4. Fermentation

Since fermentation represents a significant fraction of the sugar losses in a sugarcane biorefinery and several weaknesses of the distillation process (high energy consumption, high vinasse production) are a result of the fermentation, alternative configurations of fermentation been investigated. Among the several options available, low temperature fermentation and vacuum extractive fermentation have been evaluated (Dias et al., 2012b; Palacios-Bereche et al., 2014b). The low temperature fermentation is based on the cooling of fermentation vats to temperatures from 28 to 30 °C, what decreases yeast inhibition towards substrate and product, allowing the use of more concentrated feed and the production of wine with higher ethanol content. The vacuum extractive fermentation is based on the removal of ethanol from the fermentation reactor simultaneously to its production, what keeps ethanol concentration inside the reactor at low levels and provides reactor cooling, achieving similar decrease in yeast inhibitory effects as the low temperature fermentation. Dias et al. (2012b) and Palacios-Bereche et al. (2014b) have compared these process and verified that both of them allow an increase on ethanol production (due to higher conversion of sugars in the reactor), as well as reduction of vinasse output.

3.5. Distillation and dehydration

The original configuration and most of the current distillation columns employed in the sugarcane industry were essentially designed to support the purification of wine produced from the fermentation of molasses with low ethanol content (6-7 °GL), using direct steam injections as heat source instead of reboilers (surface heaters). Even though there is some thermal integration between streams in distillation, as mentioned in Section 2.2.4, there are still opportunities to reduce process steam consumption. One of them is the multiple effect operation of distillation columns, allowing thermal integration between column reboilers and condensers (Dias et al., 2011a).

As mentioned in Section 2.2.5, anhydrous ethanol production was initially based on the use of azeotropic distillation with benzene, nowadays replaced by cyclohexane. These usual configurations

of distillation and dehydration processes are characterized by high steam consumption, low automation and generation of large vinasse volumes (between 12–14 L/L of ethanol produced). Motivated by the possibility of selling surplus electricity (with consequent reduction on power and steam consumption in the process) and restrictions and cost of vinasse disposal, decreasing vinasse volumes with water recovery and improving the anhydrous ethanol quality to comply with export market requirements, the adsorption on molecular sieves has been preferred over other dehydration technologies – this process provides a significant reduction on process steam and electricity consumption, as indicated in Table 2.

Pervaporation systems have been developed and promote a considerable reduction in process steam consumption, but have not yet been implemented in the industry due to the high cost of membranes and the difficulties associated with fouling and long term performance. Recent developments have suggested that pervaporation systems may constitute the entire purification process from fermented wine to anhydrous ethanol, eliminating energy intensive distillation processes (Abels et al., 2013). Nevertheless, the commercial use of this technology remains to be developed.

3.6. Vinasse disposal

The amount of vinasse produced is influenced particularly by the ethanol content of the wine. However the type of heating used in the distillation columns (direct injection of steam or indirect heating using reboiler) is also a contributing factor: approximately 10–14 liters of vinasse per liter of ethanol are produced in direct steam injection and 6–8 liters for indirect heating. Even though this residue is comprised mainly by water, several organic and inorganic compounds originated from the sugarcane plant or the industrial process are present as well.

The main vinasse disposal method used in Brazil is based on fertirrigation of the sugarcane field (Cavalett et al., 2012). In São Paulo state the environmental regulator CETESB requires vinasse disposal as a function of the potassium content of the soil (CETESB, 2006). Other states forbid vinasse disposal in the liquid form near environmental protection areas, while other regions require the use diluted vinasse to promote soil irrigation. The amount of organic and inorganic compounds of vinasse requires special attention to the following aspects:

• Application of vinasse in the field can lead to temporary or definitive degradation of soil and contamination of groundwater, increased methane and N₂O emissions, depending on the type of soil (Carmo et al., 2013; Oliveira et al., 2013);

Table 2

Energy consumption for different dehydration technologies for production of anhydrous ethanol (CGEE, 2009).

Dehydration technology	Energy consumption			Steam pressure used in
	Steam (kg/m ³ hydrated ethanol)	Power (kWh/m ³ anhydrous ethanol)	Total (kcal/m ³ anhydrous ethanol)	
Conventional azeotropic distillation with cyclohexane	1750	-	1272.5	2.5 bar
Optimized azeotropic distillation with cyclohexane	1450	-	1062.5	2.5 bar
Cyclohexane with 3 effects	580	23	435.5	2.5 bar, vacuum and low pressure vapor
Extractive distillation (MEG)	750	15	572.5	10 bar
Adsorption on molecular sieves	550	19	432.5	10 bar/vacuum for regeneration
Pervaporation	110	34.5	124.5	2.5 bar and vacuum

- Vinasse storage in lagoons leads to rapid microbial decomposition and consequent odor formation;
- Most mills do not have an adequate system for vinasse distribution, which leads to environmental impacts like groundwater contamination;
- São Paulo state (the largest ethanol producer in Brazil) has the largest groundwater reserves of the country (Guarani and Bauru aquifers), and they are quite susceptible to contamination;
- Several mills are located close to environmental protection areas and water springs;
- Vinasse volume is expected to increase significantly in the next years, due to expansion of ethanol production;
- Vinasse distribution systems can be costly and rely on the use of fossil fuels.

In order to overcome some of these issues, sugarcane mills have been increasingly using vinasse concentration systems, in which water is removed producing a stream with up to 20–25% dry matter. The energy required for concentration derives from energy integration of the distillery: ethanol vapor obtained at column B–B1 is used as thermal energy source for multiple effect evaporators. Vinasse volume obtained in this process is 5–8 times smaller than the initial vinasse, and nutrients present in vinasse, such as potassium, can be distributed more efficiently on the sugarcane field, reducing the use of fertilizers. Water recovered from the condensates of vinasse concentration can be treated and reused in the process, for instance in the imbibition process in the juice extraction (Olivério et al., 2011).

An alternative to concentration, vinasse biodigestion promotes production of energy from the residue, simultaneously reducing its organic content but maintaining its nutrients load. Biogas produced in the process can be burnt for generation of electricity or sold for use as fuel, and biodigested vinasse could still be used in fertirrigation, but without most of the negative impacts like greenhouse gases emissions and contamination potential (Moraes et al., 2014).

3.7. Optimizing sugarcane distillery

If included in the standard distillery, process improvements described in the previous sections could result in an optimized distillery, which has some possible characteristics exemplified in Table 3.

Many Brazilian sugarcane mills have the characteristics of an optimized distillery. Improvements on the agricultural operations are expected as well, especially considering the development of no-till farming and precision agriculture, which can lead to significant gains in the sugarcane output per hectare, as well as in the amount of sugars and fibers of the sugarcane plant. Improvements in the industrial operations, as illustrated in Table 3, can lead to significant gains in ethanol production per hectare. In this subject, Cavalett et al. (2012) and Junqueira et al. (2012) quantitatively showed that optimization technologies lead to significant economic and environmental gains to the sugarcane biorefineries. A major breakthrough expected to achieve fully industrial scale in the years to come is the integration of second generation ethanol production in sugarcane biorefineries. This aspect is briefly elaborated in Section 3.8.

3.8. Integrated second generation ethanol production

Increasing concerns about the competition between biofuels and food production have been driving the investigation of using lignocellulosic materials and non-edible crops as feedstock for biofuels production (Harding and Peduzzi, 2012).

Integrating second generation ethanol production using surplus bagasse and straw in existing sugarcane first generation facilities offers several advantages in comparison with a stand-alone second generation plant: since sugarcane bagasse is already available at the processing site, using it as feedstock for second generation allows sharing of existing infrastructure (concentration, fermentation, distillation, dehydration, cogeneration and storage sections, for instance) and increasing ethanol production without expanding sugarcane cultivating area (Dias et al., 2012c). However, a reduction on

Table 3

Comparison between the main performance parameters for standard and optimized sugarcane distillery (CGEE, 2009)^a.

Parameter	Standard distillery	Optimized standard distillery
Sugarcane processed (wet basis) (ton/harvest season)	2,000,000	2,000,000
Useful days of operation	167	167
Agricultural yield (ton cane/hectare)	71.0	71.0
Sugarcane processed (wet basis) (ton/day)	11,976	11,976
Industrial yield (L anhydrous ethanol /ton cane)	85	88
Daily anhydrous ethanol production (L)	1,017,964	1,053,982
Anhydrous ethanol production (L/harvest season)	170,000,000	176,000,000
Agricultural area (hectare)	28,000	28,000
Total reducing sugars (kg/ton cane)	159	159
Fiber (kg/ton cane)	140	140
Extraction yield (%)	96.0	96.3
Fermentation yield (%)	89.26	89.70
Distillation yield (%)	99.00	99.50
Global yield (%)	82.29	85.50

^a Considering typical parameters from the Center-South sugarcane cultivating region (Brazil).

steam consumption of the process must take place, in order to provide large amounts of bagasse surplus for use as feedstock.

Improving first generation ethanol production with regards to its energy consumption (which is required for the integration of second generation ethanol production) is also beneficial for first generation and allows a more efficient use of the feedstock (Dias et al., 2012a). However, the exact amount of sugarcane bagasse available for use as feedstock for second generation, since it is already used as fuel in the conventional first generation process, must be determined through a careful analysis in order to avoid using an external fuel (such as natural gas) in the process. In addition, production of second generation ethanol from sugarcane bagasse may compete with the current production of electricity, which uses the same feedstock (Dias et al., 2011b; Macrelli et al., 2012). Computational models have been developed to allow such calculation, providing support for the decision-making process between the production of first and second generation ethanol and electricity from sugarcane (Bonomi et al., 2012; Furlan et al., 2012). The use of such models has shown that the integration of the biochemical route, based on lignocellulose pretreatment and enzymatic hydrolysis, in the optimized sugarcane mill using 50% of the straw produced in the field can increase ethanol production by as much as 40–50%, using the same cultivated area, if pentoses are also fermented to ethanol (Dias et al., 2012c, 2013). In order for this figure to be achieved, the process must be optimized regarding energy consumption and an engineered microorganism able to ferment both pentoses and hexoses must be used. If the conventional Saccharomyces cerevisiae is employed, only hexoses can be fermented to ethanol and the increase on ethanol production will be smaller (around 30%) (Dias et al., 2013).

4. Environmental aspects of first generation ethanol production

Life Cycle Assessment methodology (LCA) has been widely applied to evaluate environmental aspects of sugarcane biorefineries (Alvarenga et al., 2013; Amores et al., 2013; Cavalett et al., 2012, 2013; Dias et al., 2013; Junqueira et al., 2012; Luo et al., 2009; Ometto et al., 2009; Renó et al., 2011; Renouf et al., 2011; Rocha et al., 2014; Seabra et al., 2011; Tsiropoulos et al., 2014;). It is a recognized method for quantitative estimation of the environmental impacts of a product, good or service during its entire life cycle, from extraction of raw materials through manufacturing, commercialization logistics, use and final disposal or recycling. The ISO 14040 series provides a technically rigorous framework for carrying out LCAs (ISO, 2006a, 2006b).

In LCA, substantially broader environmental aspects can be covered, ranging from greenhouse gases (GHG) emissions and fossil resource depletion to acidification, toxicity, water and land use

aspects; hence, it is an appropriate tool for quantifying environmental impacts of a product system. However, many of them use a reduced set of impacts from the life cycle impacts assessment methodologies and focus only in specific impacts such as greenhouse gases and fossil energy demand (Macedo et al., 2008; Seabra et al., 2011). Regarding the possibilities of applying different life cycle impacts assessment methods (LCIA) for evaluating ethanol production form sugarcane, Cavalett et al. (2013) showed that the use of different LCIA methods could lead to different results on comparative environmental impacts of ethanol and gasoline, mainly when single-score indicators are applied. This study also showed that ethanol production and use presents better environmental performance than gasoline in some relevant categories such as global warming, fossil depletion, ecotoxicities, and ozone layer depletion but worse environmental performance than gasoline in the categories acidification, eutrophication, photochemical oxidation, and agricultural land use. Luo et al. (2009) also found similar results regarding the comparison of environmental impacts of ethanol from corn and gasoline using the CML LCIA method.

Rocha et al. (2014) performed a meta-analysis of the main environmental life cycle impacts and energy balance of ethanol from sugarcane in the Brazilian conditions. The analysis shows that the choices of co-products allocation method, transport distance and inventory database of the country, have significant influence on the results of the life cycle environmental performance of biofuels. In the same way, Seabra et al., (2011) verified comparative advantages of sugarcane products in relation to fossil alternatives. However, the authors observed that different methodologies to deal with co-products also influenced on the results.

Galdos et al. (2013) highlighted the importance of including black carbon emissions when calculating climate change and human health impacts related to ethanol production from sugarcane. This study quantitatively showed decreasing environmental impacts due to a technological trend, considering past, present and future scenarios for ethanol production systems in Brazil. The study showed that the phase out of sugarcane pre-harvesting burning; increased yield of sugarcane per hectare and ethanol per ton of sugarcane are the most important factors for decreasing environmental impacts per unit of ethanol produced over time. This study showed that the Brazilian sugarcane sector presents a trend of using resources more efficiently, as well as promoting good management practices that reduce its environmental impacts. In the same way, Seabra et al. (2011) evaluated the energy use and GHG emissions in the life cycle of sugar and ethanol from cane in Center-South of Brazil. They argue that there is a clear trend for the future, when the credits associated to electricity exports are expected to offset ethanol life cycle emissions. For the mid to long term, further reductions can be projected as advanced technologies for biomass utilization (e.g. biochemical conversion or gasification routes) become commercially available and are employed at significant levels in the sugarcane sector.

Many studies have shown that sugarcane agricultural phase is responsible for the majority of environmental impacts in the ethanol production system (Amores et al., 2013; Cavalett et al., 2012; Junqueira et al., 2012; Ometto et al., 2009). However, the efficiency of the industrial sugarcane processing system is highly technology dependent and has very strong influence in the environmental impacts results. When more outputs are produced using the same amount of resources and emissions, lower environmental impacts are observed per unit of output. For example, Renouf et al. (2011) performed a life cycle assessment of raw sugar, molasses, electricity (from bagasse combustion), and ethanol (from molasses) with focus on cane processing in Australian sugar mills. The study indicated that, beyond other factors, environmental impacts of sugarcane products are influenced by the nature of cane processing system (i.e., the range of products produced from the cane).

Cavalett et al. (2012) and Junqueira et al. (2012) showed that optimization technologies such as high pressure boilers, system integration for decreasing steam consumption, use of molecular sieves for ethanol dehydration and use of straw for power generation, among others, have a great potential to significant reduce the environmental impacts of sugarcane biorefineries in Brazil. Based on this study, it is possible to identify some points of improvement in the industrial process to reduce the environmental impacts of the ethanol production process. For example, control CO, NO_x and CH₄ emissions of the boilers; control ethanol losses in the distillation process, recycle water to reduce water uptake; cogenerate and export power to the maximum extent possible.

5. Look into the future

The usual Brazilian first generation mills are, in fact, biorefineries in the sense that several products, i.e. ethanol, sugar and electricity, may be produced from renewable feedstock in large scale facilities, providing significant economic return and important environmental impact reduction. This is the case for the annexed sugarcane distilleries discussed in this study. Many improvements and new advances may be proposed considering current process configurations.

At normal conditions each mole of ethanol that is produced by fermentation of sugars delivers one mole of CO_2 , and for each liter of ethanol 10–12 liters of vinasse are generated (Dias et al., 2012b). Surplus electricity is available at sugarcane mill, since it is produced using bagasse (and sometimes straw), exceeding the amount required by the process when efficient cogeneration technologies are employed (Dias et al., 2013). Bearing this mind a new conceptual process was proposed, as devised in Fig. 4.

In this conceptually designed integrated process, there is no local emission of CO_2 because it is used for algae cultivation. Additionally, a complete and efficient use of the sugarcane, including bagasse and straw, increases the amount of ethanol and electricity to be produced, depending upon the business model chosen.

Improvements on the first generation process may provide feedstock for production of second generation ethanol (from lignocellulosic materials, in this case surplus sugarcane bagasse and straw). This lignocellulosic material may be used to obtain synthesis gas (Ardila et al., 2014). From the synthesis gas mixed alcohols (including ethanol), hydrocarbons and other chemicals may be produced through chemical conversion processes (Čuček et al., 2011).

Regarding the use of CO_2 for microalgae cultivation as an alternative way to produce biodiesel and even ethanol, depending on the microalgae species, as well as on the nutrients balance, some fundamental studies have been carried out (Rios et al., 2014), including the development of alternative bioreactors that provide improved process performance (Jesus et al., 2012). The environmental benefits of such integration need to be investigated in economic terms in order to verify its potential. Integrated first and second generation ethanol production adding technologies to use the produced CO_2 have a better life cycle and carbon footprint than conventional sugarcane ethanol. However, there are challenges and obstacles such as cost, technology and environmental issues that must be



Fig. 4. Schematic diagram of integrated process of bioethanol production (Maciel Filho, 2014).

overcome. Hence, the introduction of new processing integrated technologies is crucial in promoting and implementing ethanol effectively and subsequently turning it in an environmentally, as well as economically, feasible source of liquid fuel for transportation.

The use of ethanol and sugars as feedstock for production of chemicals has also been foreseen as an alternative to improve the sustainability of the chemical industry in the years to come. Replacement of fossil resources by renewable materials is required in order for the chemical sector to achieve reduced environmental impacts and to guarantee its continuity in face of reduced oil reserves. Production of n-butanol in the sugarcane biorefinery, for instance, has been shown to significantly reduce global environmental impact categories in comparison with petrochemical routes (Dias et al., 2014; Pereira et al., in press), and production of other chemicals should follow this trend as well. Diversification of the product portfolio of sugarcane biorefineries can promote their economic competitiveness, especially when considering second generation ethanol production (Pereira et al., 2014).

6. Final comments

The Brazilian sugarcane industry, based on the joint production of sugar, ethanol and electricity, was described in this study. The main characteristics of the industrial process were provided, along with opportunities for process improvements and perspectives for the future of the sugarcane industry. The possibility of the sugarcane mill to produce both sugar and ethanol leads to low financial risk and flexibility to meet markets demand, among other factors. These aspects can be improved, adapted and replicated to other countries using new technologies and feedstock diversities being considered throughout the world.

Process improvements must be further implemented in the sugarcane industry in order to improve its competitiveness and allow, in the short-term, the integration of second generation ethanol production and other advanced technologies in conventional first generation facilities, which will offer additional benefits for the sector and reduce its environmental impacts.

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References

- Abels, C., Carstensen, F., Wessling, M., 2013. Membrane processes in biorefinery applications. J. Membr. Sci. 444, 285–317, http://dx.doi.org/10.1016/j.memsci.2013.05.030.
- Albarelli, J.Q., Ensinas, A.V., Silva, M.A., 2014. Product diversification to enhance economic viability of second generation ethanol production in Brazil: the case of the sugar and ethanol joint production. Chem. Eng. Res. Des. 92 (8), 1470–1481, http://dx.doi.org/10.1016/j.cherd.2013.11.016.
- Alonso Pippo, W., Luengo, C.A., Alonsoamador Morales Alberteris, L., Garzone, P., Cornacchia, G., 2011. Energy recovery from sugarcane-trash in the light of 2nd generation biofuel. Part 2: socio-economic aspects and techno-economic Analysis. Waste Biomass Valorization 2 (3), 257–266, http://dx.doi.org/10.1007/s12649-011-9069-3.
- Alvarenga, R.A.F., Dewulf, J., De Meester, S., Wathelet, A., Villers, J., Thommeret, R., Hruska, Z., 2013. Life cycle assessment of bioethanol-based PVC. Part 1: attributional approach. Biofuels Bioprod. Biorefin. 7, 386–395, http://dx.doi.org/ 10.1002/bbb.1405.
- Amores, M.J., Mele, F.D., Jiménez, L., Castells, F., 2013. Life cycle assessment of fuel ethanol from sugarcane in Argentina. Int. J. Life Cycle Assess. 18, 1344–1357, http://dx.doi.org/10.1007/s11367-013-0584-2.
- Ardila, Y.C., Efren, J., Figueroa, J., Lunelli, B.H., Maciel Filho, R., Maciel, M.R.W., 2014. Simulation of ethanol production via fermentation of the synthesis gas using aspen plus TM. Chem. Eng. Trans. 37 (2), 637–642, http://dx.doi.org/ 10.3303/CET1437107.
- Bonomi, A., Mariano, A.P., Jesus, C.D.F., Franco, H.C.J., Cunha, M.P., Dias, M.O.S., Chagas, M.F., Cavalett, O., Mantelatto, P.E., Filho, R. M., Junqueira, T.L., Cardoso, T.F., 2012. The Virtual Sugarcane Biorefinery (VSB): 2011 Report. Campinas, São Paulo: Brazilian Center for Research in Energy and Materials (CNPEM), Brazilian Bioethanol Science and Technology Laboratory (CTBE), Internal Report. Available at http://ctbe.cnpem.br/wp-content/uploads/2014/07/vsb-report-2011.pdf (accessed February 2013).

- Cardoso, T.D.F., Cavalett, O., Chagas, M.F., Morais, E.R. De, Nunes, J.L., Franco, H.C.J., Galdos, M.V., Scarpare, F.V., Braunbeck, O.A., Cortez, L.A.B., Bonomi, A., 2013. Technical and economic assessment of trash recovery in the sugarcane bioenergy. Sci. Agric. 70 (5), 353–360, http://dx.doi.org/10.1590/S0103-90162013000500010.
- Carmo, J.B., Fisolo, S., Zotelli, L.C., Sousa Neto, E.R., Pitombo, L.M., Duarte-Neto, P.J., Vargas, V.P., Andrade, C.A., Gava, G.J.C., Rossetto, R., Cantarella, H., Neto, A.E., Martinelli, L.A., 2013. Infield greenhouse gas emissions from sugarcane soils in Brazil: effects from synthetic and organic fertilizer application and crop trash accumulation. GCB Bioenergy 5, 267–280, http://dx.doi.org/10.1111/j.1757-1707.2012.01199.x.
- Cavalett, O., Junqueira, T.L., Dias, M.O.S., Jesus, C.D.F., Mantelatto, P.E., Cunha, M.P., Franco, H.C.J., Cardoso, T.F., Maciel Filho, R., Rossell, C.E.V., Bonomi, A., 2012. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. Clean Technol. Environ. Policy 14, 399–410.
- Cavalett, O., Chagas, M.F., Seabra, J.E.A., Bonomi, A., 2013. Comparative LCA of ethanol versus gasoline in Brazil using different LCIA methods. Int. J. Life Cycle Assess. 18 (3), 647–658, http://dx.doi.org/10.1007/s11367-012-0465-0.
- CETESB, 2006. Vinasse criteria and requirements for disposal on cultivated land. Available at (http://www.cetesb.sp.gov.br/ Tecnologia/camaras/P4_231.pdf) (accessed November 2014).
- CGEE. Bioetanol combustível: uma oportunidade para o Brasil. Centro de Gestão e Estudos Energéticos (CGEE), UNICAMP, 2009, isbn:978-85-60755-15-8.
- Chandel, A.K., Junqueira, T.L., Morais, E.R., Gouveia, V.L.R., Cavalett, O., Rivera, E.C., Geraldo, V.C., Bonomi, A., da Silva, S.S., 2014. Techno-economic analysis of second-generation ethanol in Brazil: competitive, complementary aspects with firstgeneration ethanol. In: da Silva, Silvio Silvério, Chandel, Anuj Kumar (Eds.), Biofuels in Brazil.
- Chavez-Rodriguez, M.F., Mosqueira-Salazar, K.J., Ensinas, A.V., Nebra, S.A., 2013. Water reuse and recycling according to stream qualities in sugar–ethanol plants. Energy Sustain. Dev. 17 (5), 546–554, http://dx.doi.org/10.1016/j.esd.2013.08.003.
- Čuček, L., Martín, M., Grossmann, I.E., Kravanja, Z., 2011. Energy, water and process technologies integration for the simultaneous production of ethanol and food from the entire corn plant. Comput. Chem. Eng. 35 (8), 1547–1557, http://dx.doi.org/ 10.1016/j.compchemeng.2011.02.007.
- Dias, M.O.S., Modesto, M., Ensinas, A.V., Nebra, S.A., Maciel Filho, R., Rossell, C.E.V., 2011. Improving bioethanol production from sugarcane: evaluation of distillation, thermal integration and cogeneration systems. Energy 36, 3691–3703, http://dx.doi.org/ 10.1016/j.energy.2010.09.024.
- Dias, M.O.S., Cunha, M.P., Jesus, C.D.F., Rocha, G.J.M., Pradella, J.G.C., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2011. Second generation ethanol in Brazil: can it compete with electricity production? Bioresour. Technol. 102, 8964–8971, http://dx.doi.org/ 10.1016/j.biortech.2011.06.098.
- Dias, M.O.S., Junqueira, T.L., Jesus, C.D.F., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2012. Improving second generation ethanol production through optimization of first generation production process from sugarcane. Energy 43, 246–252, http://dx.doi.org/10.1016/j.energy.2012.04.034.
- Dias, M.O.S., Junqueira, T.L., Jesus, C.D.F., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2012. Improving bioethanol production comparison between extractive and low temperature fermentation. Appl. Energy 98, 548–555, http://dx.doi.org/10.1016/ j.apenergy.2012.04.030.
- Dias, M.O.S., Junqueira, T.L., Cavalett, O., Cunha, M.P., Jesus, C.D.F., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2012. Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. Bioresour. Technol. 103 (1), 152–161, http://dx.doi.org/10.1016/j.biortech.2011.09.120.
- Dias, M.O.S., Junqueira, T.L., Cavalett, O., Cunha, M.P., Jesus, C.D.F., Mantelatto, P.E., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2013. Cogeneration in integrated first and second generation ethanol from sugarcane. Chem. Eng. Res. Des. 91 (8), 1411–1417, http://dx.doi.org/10.1016/j.cherd.2013.05.009.
- Dias, M.O.S., Pereira, L.G., Junqueira, T.L., Pavanello, L.G., Chagas, M.F., Cavalett, O., Maciel Filho, R., Bonomi, A., 2014. Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part I: Integration to a first generation sugarcane distillery. Chem. Eng. Res. Des. 92 (8), 1441–1451, http://dx.doi.org/10.1016/j.cherd.2014.04.030.
- Furlan, F.F., Costa, C.B.B., Fonseca, G.D.C., Soares, R.D.P., Secchi, A.R., Cruz, A.J.G., Giordano, R.D.C., 2012. Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling. Comput. Chem. Eng. 43, 1–9, http://dx.doi.org/10.1016/j.compchemeng.2012.04.002.
- Galdos, M., Cavalett, O., Seabra, J.E.A., Nogueira, L.A.H., Bonomi, A., 2013. Trends in global warming and human health impacts related to Brazilian sugarcane ethanol production considering black carbon emissions. Appl. Energy 104, 576–582, http://dx.doi.org/10.1016/j.apenergy.2012.11.002.
- Harding, R., Peduzzi, P., 2012. The end to cheap oil: a threat to food security and an incentive to reduce fossil fuels in agriculture. Environ. Dev. 3, 157–165, http://dx.doi.org/10.1016/j.envdev.2012.05.008.
- ISO, 2006. ISO International Standard 14040: Environmental management Life cycle assessment Principles and framework. International Organization for Standardization, Geneva, Switzerland28.
- ISO, 2006. ISO International Standard 14044: Environmental management Life cycle assessment Requirements and guidelines. International Organization for Standardization, Geneva, Switzerland54.
- Jesus, S.S., Arias, E.L.M., Santana, A., Maciel Filho, R., 2012. Estimation hydrodynamic parameters and mass transfer in a stirred airlift bioreactor using viscous fluids. New Biotechnol. (Print) 29, S213, http://dx.doi.org/10.1016/j.nbt.2012.08.597.
- Junqueira, T.L., Dias, M.O.S., Maciel Filho, R., Wolf Maciel, M., Rossell, C.E.V., 2009. Simulation of the azeotropic distillation for anhydrous bioethanol production: study on the formation of a second liquid phase. Comput. Aided Chem. Eng. 27, 1143–1148, http://dx.doi.org/10.1016/S1570-7946(09)70411-0.
- Junqueira, T.L., Dias, M.O.S., Cavalett, O., Jesus, C.D.F., Cunha, M.P., Rossell, C.E.V., Maciel Filho, R., Bonomi, A., 2012. Economic and environmental assessment of integrated 1st and 2nd generation sugarcane bioethanol production evaluating different 2nd generation process alternatives. Comput. Aided Chem. Eng. 30, 177–181, http://dx.doi.org/10.1016/B978-0-444-59519-5.50036-8.
- Leal, M.R.L.V., Walter, A.S., Seabra, J.E.A., 2013. Sugarcane as an energy source. Biomass Convers. Biorefin. 3 (1), 17–26, http://dx.doi.org/10.1007/s13399-012-0055-1.
- Luo, L., van der Voet, E., Huppes, G., 2009. Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol. Int. J. Life Cycle Assess. 14, 529–539, http://dx.doi.org/10.1007/s11367-009-0112-6.

- Macedo, I.C., Seabra, J.E.A., Silva, J., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. Biomass Bioenergy 32 (7), 582–595, http://dx.doi.org/ 10.1016/j.biombioe.2007.12.006.
- Maciel Filho, R., 2014. An integrated process for total bioethanol production and zero CO₂ emission. In: Proceedings of the Fapesp Bioenergy Program. Available at http://media.fapesp.br/bv/uploads/publicacoes/pasta_bioen_jun2012_124.pdf (accessed on November 2014).
- Macrelli, S., Mogensen, J., Zacchi, G., 2012. Techno-economic evaluation of 2nd generation bioethanol production from sugar cane bagasse and leaves integrated with the sugar-based ethanol process. Biotechnol. Biofuels 5 (1), 22, http://dx.doi.org/ 10.1186/1754-6834-5-22.
- MAPA, 2014. Brazilian Sugar Exports. Available at (http://www.agricultura.gov.br/arq_editor/file/Desenvolvimento_Sustentavel/ Agroenergia/estatisticas/comercio_exterior_brasileiro/acucar/2.pdf) (accessed November 2014).
- Moraes, B.S., Junqueira, T.L., Pavanello, L.G., Cavalett, O., Mantelatto, P.E., Bonomi, A., Zaiat, M., 2014. Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? Appl. Energy 113, 825–835, http://dx.doi.org/10.1016/j.apenergy.2013.07.018.
- Oliveira, B.G., Carvalho, J.L.N., Cerri, C.E.P., Cerri, C.C., Feigl, B.J., 2013. Soil greenhouse gas fluxes from vinasse application in Brazilian sugarcane areas. Geoderma 200–201, 77–84, http://dx.doi.org/10.1016/j.geoderma.2013.02.005.
- Olivério, J.L., Carmo V.C., Gurgel M.A., 2010. The DSM dedini sustainable mill: a new concept in designing complete sugarcane mills. In: Proceedings of the International Society of Sugar Cane Technologists, Vol. 27, Mexico.
- Olivério, J.L., Boscariol, F.C., Mantelatto, P.E., César, A.R.P., Ciambelli, J.R.P., Gurgel, M.N.A., Souza, R.T.G., 2011. Integrated production of organomineral biofertiliser (BIOFOM[®]) using by-products from the sugar and ethanol agro-industry, associated with the cogeneration of energy. Sugar Tech 13, 17–22, http://dx.doi.org/10.1007/s12355-011-0069-1.
- Ometto, A.R., Hauschild, M.Z., Roma, W.N.L., 2009. Lifecycle assessment of fuel ethanol from sugarcane in Brazil. Int. J. Life Cycle Assess. 14, 236–247, http://dx.doi.org/10.1007/s11367-009-0065-9.
- Palacios-Bereche, R., Ensinas, A.V., Modesto, M., 2014. Extraction process in the ethanol production from sugarcane a comparison of milling and diffusion, *Chem. Eng. Trans.* 39, 1519–1524, http://dx.doi.org/10.3303/CET1439254.
- Palacios-Bereche, R., Ensinas, A., Modesto, M., Nebra, S.A., 2014. New alternatives for the fermentation process in the ethanol production from sugarcane: extractive and low temperature fermentation. Energy 70 (1), 595–604, http://dx.doi.org/ 10.1016/j.energy.2014.04.032.
- Pellegrini, L.F., Oliveira Júnior, S., 2011. Combined production of sugar, ethanol and electricity: thermoeconomic and environmental analysis and optimization. Energy 36 (6), 3704–3715, http://dx.doi.org/10.1016/j.energy.2010.08.011.
- Pereira, L.G., Chagas, M.F., Dias, M.O.S., Cavalett, O., Bonomi, A., 2015. Life cycle assessment of butanol production in sugarcane biorefineries in Brazil. J. Clean. Prod. http://dx.doi.org/10.1016/j.jclepro.2014.01.059. (in press).
- Pereira, L.G., Dias, M.O.S., Junqueira, T.L., Chagas, M.F., Cavalett, O., Maciel Filho, R., Bonomi, A., 2014. Production of Butanol and Other High Valued Chemicals Using Ethanol as Feedstock Integrated to a First and Second Generation Sugarcane Distillery. Chem. Eng. Trans. 37, 805–810, http://dx.doi.org/10.3303/CET1437135.
- Renó, M.L.G., Lora, E.E.S., Palacio, J.C.E., Venturini, O., Buchgeister, J., Almazan, O.C., 2011. A LCA (life cycle assessment) of the methanol production from sugarcane bagasse. Energy 36, 3716–3726, http://dx.doi.org/10.1016/j.energy.2010.12.010.
- Renouf, M.A., Pagan, R.J., Wegener, M.K., 2011. Life cycle assessment of Australian sugarcane products with a focus on cane processing. Int. J. Life Cycle Assess. 16, 125–137, http://dx.doi.org/10.1007/s11367-010-0233-y.
- Rios, L.F., Klein, B.C., Luz, L.F., Maciel Filho, R., Wolf Maciel, M.R., 2014. Nitrogen starvation for lipid accumulation in the microalga species *Desmodesmus* sp. Appl. Biochem. Biotechnol. http://dx.doi.org/10.1007/s12010-014-1283-6.
- Rocha, M.H., Capaz, R.S., Lora, E.E.S., Nogueira, L.A.H., Leme, M.M.V., Renó, M.L.G., del Olmo, O.A., 2014. Life cycle assessment (LCA) for biofuels in Brazilian conditions: a meta-analysis. Renew. Sustain. Energy Rev. 37, 435–459, http://dx.doi.org/ 10.1016/j.rser.2014.05.036.
- Seabra, J.E.A., Macedo, I.C., 2011. Comparative analysis for power generation and ethanol production from sugarcane residual biomass in Brazil. Energy Policy 39 (1), 421–428, http://dx.doi.org/10.1016/j.enpol.2010.10.019.
- Seabra, J.E.A., Macedo, I.C., Chum, H.L., Faroni, C.E., Sarto, C.A., 2011. Life cycle assessment of Brazilian sugarcane products: GHG emissions and energy use. Biofuels Bioprod. Biorefin. 5, 519–532, http://dx.doi.org/10.1002/bbb.
- Serra, L., Lozano, M.A., Ramos, J., Ensinas, A.V., Nebra, S.A., 2009. Polygeneration and efficient use of natural resources. Energy 34 (5), 575–586, http://dx.doi.org/10.1016/j.energy.2008.08.013.
- Soccol, C.R., Vandenberghe, L.P.D.S., Medeiros, A.B.P., Karp, S.G., Buckeridge, M., Ramos, L.P., Pitarelo, A.P., Ferreira-Leitão, V., Gottschalk, L.M.F., Ferrara, M.A., Bon, E.P.S., Moraes, L.M.P., Araújo, A., Torres, F.A.G., 2010. Bioethanol from lignocelluloses: status and perspectives in Brazil. Bioresour. Technol. 101 (13), 4820–4825, http://dx.doi.org/10.1016/j.biortech.2009.11.067.
- Tsiropoulos, I., Faaij, A.P.C., Seabra, J.E.A., Lundquist, L., Schenker, U., Briois, J.F., Patel, M.K., 2014. Life cycle assessment of sugarcane ethanol production in India in comparison to Brazil. Int. J. Life Cycle Assess. 19, 1049–1067, http://dx.doi.org/ 10.1007/s11367-014-0714-5.