LCA FOR RENEWABLE RESOURCES

Life cycle assessment of fuel ethanol from sugarcane in Argentina

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Abstract
Purpose The production of bioethanol in Argentina is based
on the sugarcane plantation system, with extensive use of
agricultural land, scarce use of fertilizers, pesticides, and
artificial irrigation, and burning of sugarcane prior to
harvesting. The objective of this paper is to develop a life
cycle assessment (LCA) of the fuel ethanol from sugarcane in
Tucumán (Argentina), assessing the environmental impact
potentials to identify which of them cause the main impacts.
Methods Our approach innovatively combined knowledge
about the main impact pathways of bioethanol production
with LCA which covers the typical emission-related impact
categories at the midpoint life cycle impact assessment. Real
data from the Argentinean industry subsystems have been
used to perform the study: S1—sugarcane production,
S2—milling process, S3—sugar production, and S4—ethanol
production from molasses, honey, or sugarcane juice.
Results and discussion The results are shown in the three
alternative pathways to produce bioethanol. Different impact
categories are assessed, with global warming potential (GWP)
having the highest impact. So, the production of 1 kg of
ethanol from molasses emitted 22.5 kg CO_2 (pathway 1),
19.2 kg CO_2 from honey (pathway 2), and 15.0 kg CO_2 from
sugarcane juice (pathway 3). Several sensitivity analyses to
study the variability of the GWP according to the different
cases studied have been performed (changing the agricultural
yield, including economic and calorific allocation in sugar
production, and modifying the sugar price).
Conclusions Agriculture is the subsystem which shows the
highest impact in almost all the categories due to fossil fuel
consumption. When an economic and calorific allocation is
considered to assess the environmental impact, the value is
lower than when mass allocation is used because ethanol is
relatively cheaper than sugars and it has higher calorific value.

Keywords Argentina · Bioethanol · Life cycle assessment ·
Sugarcane

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1 Introduction

The concern about "sustainability" (Brundtland 1987) has
increased in the last decades. Nowadays, there is a rising
awareness about the future reduction of fossil energy re-
sources, such as those coming from oil. Thus, renewable
fuels have gained wider interest in the recent past,
bioethanol being one of the most successful examples of a
shift from fossil fuels to bio-based fuels.

The use of ethanol in vehicles was first proposed by H.
Ford (1896). After the oil crisis, ethanol became more
popular and oil-importing countries were forced to develop
alternative fuel programs to reduce their dependence on oil.
Over the last decades, vast investments, government spon-
sorship, and tax incentives made Brazil and USA the world
leaders in ethanol production. Nowadays, many countries
have launched programs to replace gasoline by ethanol in

the midterm (Olsson 2007). Following this trend, Argentina published Law 26.093 in 2006, which provides the framework for the investment, production, and marketing of biofuels, which focused primarily on conventional biofuels: biodiesel from soybean oil and bioethanol from sugarcane. This framework, which became active in 2010, establishes 5 % as the minimum bioethanol content in gasoline. The main goal is to reduce emissions of carbon dioxide and other greenhouse gases (GHG), to diversify the supply of energy, and to promote the development of rural areas, especially in benefit of small-sized and medium-sized agricultural producers.

So far, the Argentinean ethanol industry is based exclusively on sugarcane, and its primary focus is the domestic market. The sugar industry welcomed the alternative to direct sugarcane surpluses to the profitable local ethanol market rather than exporting sugar. Moreover, Argentina has abundant natural resources, a very efficient agricultural production sector, good processing and export infrastructures, and a suitable human capital (Joseph 2010).

The fuel ethanol production model is based mostly on a sugarcane plantation system with extensive use of agricultural land, scarce use of fertilizers, pesticides, and artificial irrigation, and burning of sugarcane prior to harvesting. A scheme of the production process from sugarcane to ethanol can be seen in Fig. 1. Ethanol in Argentina is currently produced by 15 sugar mills located in the northwest of the country that use sugar molasses as main feedstock. Almost all sugar mills produce electricity from bagasse for their own use, but there are four sugar mills which cogenerate electricity and sell the excess to the electrical grid. Argentina needs to expand its sugarcane industry in order to meet the official requirements. Production in 2011 is projected at 280,000 m^3 of bioethanol (Joseph 2010).

Argentinean bioethanol producers will need to study the environmental performance of their product in order to comply with the sustainability criteria (Farrell et al. 2006). Due to the potential of Argentina to produce bioethanol, this work constitutes a baseline to analyze the environmental impact and country-specific pathways by estimating the GHG emissions and other impact potentials. Sugarcane will play an important role, given its resistance, rapid growth, and uptake capacity for atmospheric carbon. However, Argentina, as a sugarcane-based biofuel producer, is likely to be not competitive from the environmental point of view, unless specific measures are implemented. These measures include avoiding deforestation, applying reduced tillage and crops successions, using low ecotoxicity pesticides, and improving the sustainable methods to treat the huge volumes of vinasses generated. Moreover, there are other arising drawbacks such as land competition with food and environmental impact associated with the transport sector. In addition to this, the rapid expansion of ethanol production/consumption has affected the international market of sugar, an important coproduct of ethanol. Such a complex environment poses significant challenges for practitioners and researchers.

In particular, one of the key issues that have not been tackled so far and is very timely to perform is environmental impact assessment of the bioethanol production in Argentina from a life cycle assessment (LCA) perspective, as what has been done in the cases of Argentinean biodiesel production (Asal et al. 2006; Panichelli et al. 2009; Tomei and Upham 2009). The LCA approach will shed light on some of these problems, but not on all of them. For example, it will be able to show improvement opportunities on GHG, acidification, and eutrophication emissions; however, land and water use and issues related to indirect land use changes and competition with food products do not fit well into the LCA framework. These last categories require a broader approach (Luo et al. 2009). The LCA studies conducted in Argentina on bioethanol production have been incipient, as can be confirmed from the review article by Chauhan et al. (2011). With regards to the LCA applied to the sugarcane-based ethanol, some relevant contributions that appeared in the recent literature referred to production in other countries, for instance, Australia (Renouf et al. 2011), Brazil (Cavalett et al. 2012; Luo et al. 2009; Pereira and Ortega 2010; Ometto et al. 2009; Seabra et al. 2011), Mexico (García et al. 2011), and Thailand (Nguyen and Gheewala 2008). None of these studies are comparable enough to the case of Argentina as they analyze specific geographic situations and practices; however, some general trends can be derived from the results of these studies, which will be mentioned in Section 4.

There are a number of reasons to assess the Argentinean sugarcane-based ethanol from an LCA perspective: (1) Fuel ethanol made from sugarcane is based on renewable resources in contrast to other types of fuel; (2) sugarcane leads to one of the main economic activities in the rural areas of the Argentinean Northwest, with many environmental and social implications; (3) a country-specific approach to LCA is crucial when evaluating the environmental impacts of bioenergy systems: local conditions, such as agricultural practices, land use changes, and transport infrastructures, will have a major impact on the environmental performance of the system (Panichelli et al. 2009); (4) many steps in the life cycle of Argentinean fuel ethanol have remained unchanged for a long time, so the improvement potential is substantial; it is possible to cogenerate electricity from the solid waste and to recycle some of the waste streams; and (5) Argentinean ethanol producers will need to evaluate the environmental performances of their product in order to comply with sustainability criteria being developed.

Therefore, the goal of this paper is to present the LCA of the fuel ethanol from sugarcane in Tucumán (Argentina), assessing the environmental impact potentials, in order to identify the activities of the life cycle, which cause the main

impacts. Also, some guidelines for environmental improvements will be indicated. Different scenarios will be analyzed (the current situation and two hypothetical scenarios), and a sensitivity analysis of some parameters will be performed.

2 Methods

2.1 Overview

The methodological structure for this LCA study was built according to the International Standardization Organization (ISO) series 14040 and 14044 on LCA (ISO 2006a, b). We perform a "cradle-to-gate" analysis that embraces all the activities of the network, starting from the extraction of raw materials (agricultural stages) and ending with the products at the "gate" of the manufacturing plants (sugar mills and distilleries). The system description and inventory data are valid for sugarcane-based bioethanol in Argentinean Northwest (country-specific approach) and for the time framework 2000–2005, as technologies, prices, and production methods are assumed to change in the midterm.

The life cycle inventory (LCI) data for our problem were obtained from different sources. With regard to the agricultural stages, we collected data from local agricultural companies and governmental organizations (Pérez et al. 2007). For the industrial stages, we considered standard mass and energy balance coefficients taken from typical sugar mills and distilleries. Data gaps have been covered using specialized literature, handbooks, and databases; all cited when showing the LCI results. These data have been partially used in other works of the authors (Mele et al. 2011; Kostin et al. 2011, 2012) in which the objective is rather to optimize the ethanol supply chain than perform a detailed LCA study.

Life cycle impact assessment (LCIA) was performed on the EcoInvent® 2.2 database (Swiss Centre for Life-Cycle Inventories 2010). The LCIA of this study has been done using the CML2001 (Centre for Environmental Studies 2001), the most widely applied midpoint LCIA method, covering the following emission-related impact categories: acidification potential (AP), global warming potential (GWP), eutrophication potential (EP), photochemical oxidation (PHO), depletion of abiotic resources (DAR), ozone depletion potential (ODP), freshwater aquatic ecotoxicity (FWAET), and terrestrial ecotoxicity (TET); all available in the EcoInvent® 2.2 database.

The functional unit (FU) of this study is 1 kg of fuel anhydrous ethanol produced. The results are calculated assuming the average sugarcane productivity of 67 t sugarcane/ha in 1 year crop cultivation. This value is based on the average yield from 2000 to 2005 harvesting periods in the province of Tucumán (Pérez et al. 2007).

The system boundaries have been expanded where possible, including the impact associated with the production of raw materials (e.g., fertilizers, lime, sulfuric acid, etc.). In line with common LCA practice, we have not considered the impact associated with the production of capital equipment. Moreover, as the study focuses on the production stages, the system boundaries do not include storage and transportation tasks after production.

Although the ISO norm recommends subdividing the system or performing system expansion so as to avoid allocation, some allocation has been used when it was strictly necessary. Sensitivity analysis was performed for allocation based on mass, price, and calorific value to evaluate the variability of results with regard to this key methodological parameter. The allocation method based on price has been considered in accordance with the EcoInvent database for bioenergy products (Jungbluth et al. 2007) where allocation of environmental impacts between coproducts is based on the respective prices of coproducts. Different authors of comparable studies also conducted mass allocation by mass (Luo et al. 2009; Ometto et al. 2009; Seabra et al. 2011), energy content (García et al. 2011), and price (Cavalett et al. 2012; García et al. 2011; Nguyen and Gheewala 2008).

Emissions from land use other than direct deforestation are excluded due to lack of data. Agricultural and industrial data are, as much as possible, specific to the Argentinean context. However, since the production of bioethanol in Argentina so far remains a secondary activity, data are not fully available nor gathered into a unified database. Therefore, some data are based on average technologies and they are opportunely referenced.

2.2 System description and inventory data

The system under study is the Argentinean standard fuel anhydrous ethanol industry (see Fig. 1). The overall system has been divided into four subsystems: S1—agriculture, S2—milling, S3—sugar production, and S4—ethanol production, which are combined to give the production pathways considered in this study.

The reference case (RC) studied in this paper includes three main pathways according to the technology used. These pathways have in common that they include the same type of subsystems (agriculture and milling), but they differ in the technologies used to produce sugar and ethanol, as shown in Fig. 2.

–   Pathway 1 produces ethanol from molasses. The sugarcane is milled. Then, the cane juice is processed with technology T1, and finally, the resulting molasses are converted into ethanol in a distillery type T3.
–   Pathway 2 produces ethanol from honey obtained in a manufacturing process that uses technology T2. Honey is converted into ethanol in a distillery using technology T4.

Fig. 1 Productive system used in Argentina to produce ethanol from sugarcane
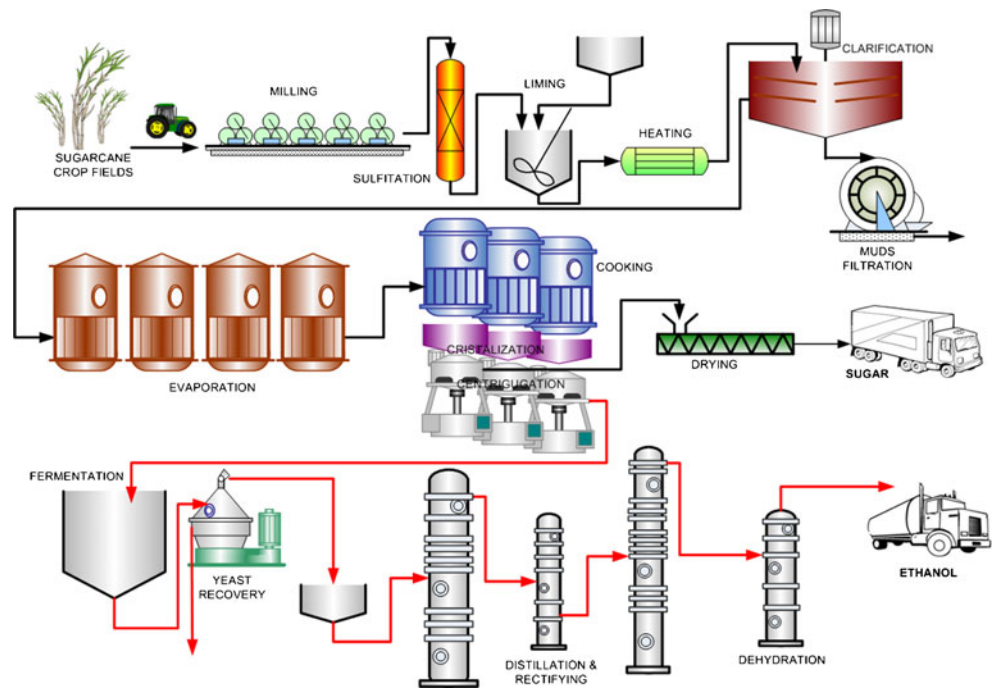
- Pathway 3 produces ethanol directly from sugarcane juice coming from sugarcane milling. Ethanol is obtained through technology T5. This pathway does not produce sugar.

It is worth mentioning that these pathways are standard in the worldwide sugarcane industry. Countries apply one of them according to their preferences. In Brazil, P3—autonomous distillery—is very common (Cavalett et al. 2012; Seabra et al. 2011), whereas in Argentina, this pathway is practically inexistent. In Mexico, García et al.

(2011) considered the three options in the study, while in Thailand, Nguyen and Gheewala (2008) claim that ethanol from molasses (P1) is the most common pathway. Apart from that, there is a big variability in the way the countries implement these pathways, which is mostly related to the way in which each country drives the agricultural practices and supplies energy to the process (e.g., bagasse, crop trash, natural gas, fuel oil, different mixtures, etc.).

Figure 3a–c shows a detailed input–output diagram for the three pathways described previously. The subsystem

Fig. 2 Schematic of the three pathways considered in the RC
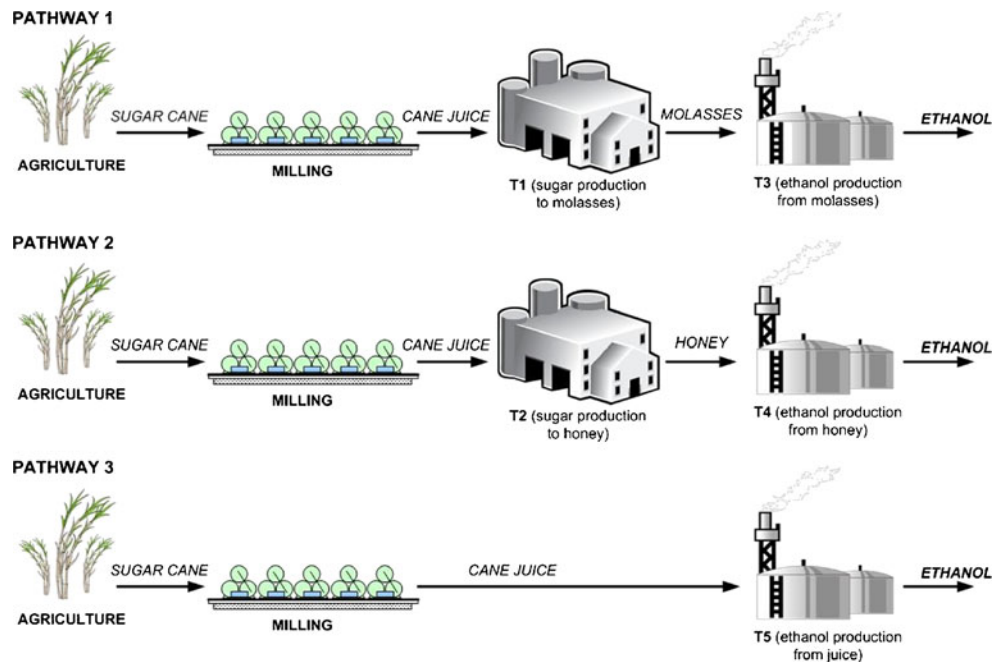
Agriculture involves all the activities related to sugarcane planting, growing, and harvesting, as well as transportation to sugar mills. Sugarcane is regarded as the main product of these activities. Sugarcane production in the province of Tucumán (Argentina) is characterized by the partial use of synthetic fertilizers, pesticides, and semi-mechanized cultivation and harvesting. Although sugarcane is allowed to grow with the same stalk five times after cutting, the annual renewal percentage, as well as the involved activities, has not been taken into account in this study. We have taken the worst case of planting for the first time, as described by Caro et al. (2009). Trucks to transport ratoons and tractors to open trenches on the field are the equipment used in the manual plantation.

Regarding agrochemical applications, tractors are used for pesticide and fertilizer applications in the total sugarcane area. For the fertilizer and pesticide application emissions, the consideration that the soil is part of the technosphere was used, in which only emissions that come out of the production system ground level and that interfere with the air or water quality were assessed. In Argentina, most of the pesticides and fertilizers are imported. The production processes for these inputs have been included into the system boundaries. Sugarcane nitrogen fertilizer is applied as urea (200 kg/ha), and phosphorus fertilizer is applied as triple super phosphate in low doses of about 24 kg/ha. Other fertilizers have not been included due to lack of data and

low use. No K fertilizer is applied in the sugarcane production in Tucumán. Among the pesticides, the most common are insecticides like permethrin and herbicides like glyphosate. Due to the lack of regional information, nitrogen oxides and ammonia emissions to air, nitrate and phosphorous emissions to groundwater, and phosphorous emissions to surface water were all estimated from Renouf et al. (2008). The ash from bagasse combustion and the filter cake from juice clarification (see the subsystems *Milling* and *Sugar Production* in Fig. 3) are transported to the fields by truck and disposed in the soil to substitute some of the synthetic fertilizers used.

In Tucumán, artificial irrigation is not significant, while the use of vinasses, a residue of ethanol distillation, for irrigation is not a generalized practice. Harvesting is carried out every year in the total area from May to November (*zafra*). Sugarcane harvesting in the province of Tucumán is carried out mainly with machines. Although it is currently penalized by law, burning before harvesting to facilitate cutting has been considered to be used on 50 % of the total area. After being cut, the sugarcane is transported with trucks to the industrial process. In the agricultural stages, transport distances are based on an average distance of 50 km. Diesel consumption in agricultural processes was converted into inputs of the subsystem *Agriculture* according to EcoInvent® (Nemecek et al. 2007). Diesel consumption for agricultural activities: plantation, cultivation, harvesting, and transport have been calculated based on data from Caro et al. (2009). Biogenic
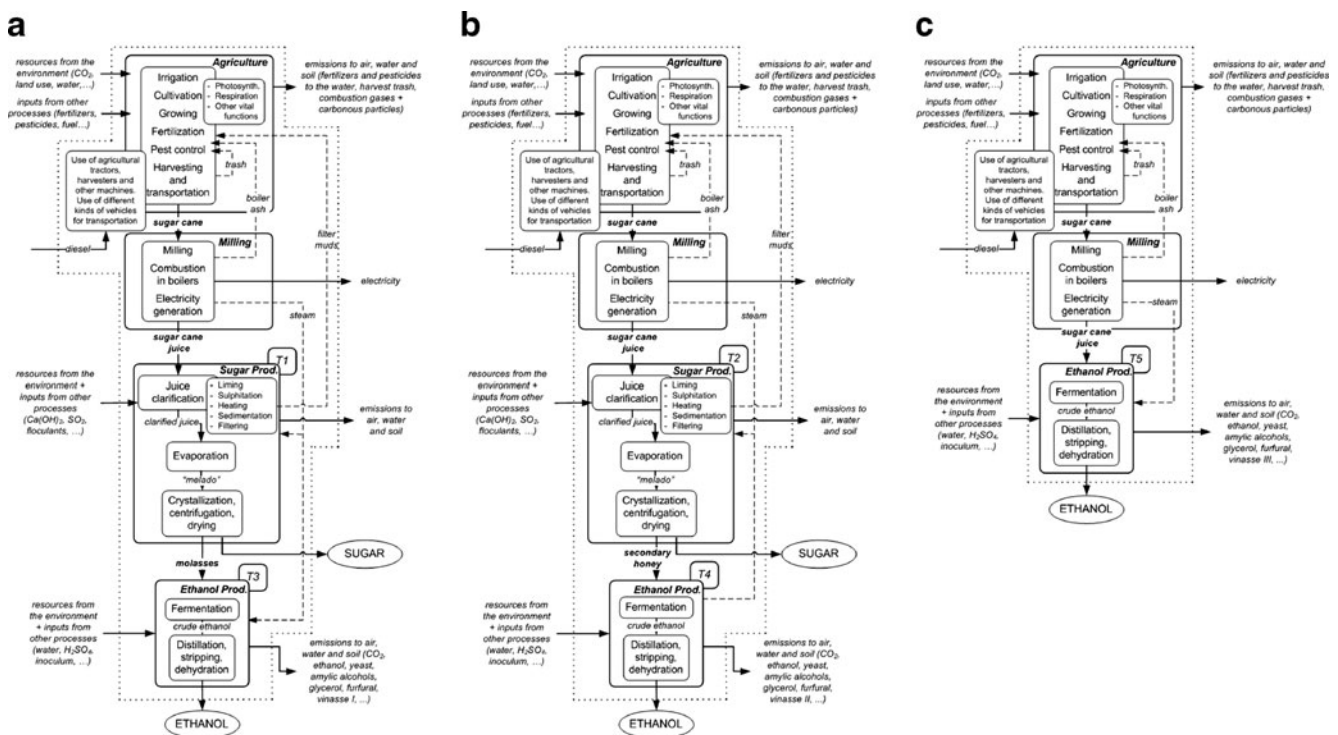
Fig. 3 System diagrams for ethanol production from different production pathways: **a** ethanol production from molasses (T1 and T3), **b** ethanol production from honey (T2 and T4), and **c** ethanol production from juice (T5)

CO_2 uptake (0.819 kg/kg sugarcane) is estimated from the carbon balance. Table 1 shows the inventory values for the subsystem *Agriculture*. All the entries for this table are referred to 1 kg of sugarcane as a reference flow.

The subsystem *Milling* involves washing of the harvested sugarcane, transport by conveyor belts to the mills, milling to extract sugarcane juice, and burning of the lignocellulosic residue of sugarcane (bagasse) in boilers to generate steam and electricity in cogeneration plants. The electricity production satisfies all the sugar mill requirements. The excess energy is exported to the public network. Sugarcane juice is the main product of this subsystem. Exported electricity has been regarded as a coproduct whose allocation has been solved by expanding the system boundaries and retrieving the necessary data from the EcoInvent® database. In that case, we have used the electric mix from Argentina according to the relative contribution of 45 % natural gas, 11 % oil, 33 % hydropower, 6 % nuclear, 1 % hard coal, 1 % biomass, and 3 % imported energy from Brazil. Table 2 shows the inventory values for the subsystem *Milling*.

The subsystem *Sugar Production* includes the purification and concentration of sugarcane juice to obtain dry sugar crystals. First, the juice is acidified with SO_2 and neutralized with lime slurry to precipitate the impurities. Then, it is heated to diminish juice viscosity and the solubility of the calcium salts generated. Finally, the juice enters a series of decanters where solid materials are separated from the juice. The solid residue of the clarification is filtered to recover some juice, producing a filter mud (*cachaza*), which is transported to the crop fields as a

fertilizer. Clarified juice is concentrated in multi-effect continuous evaporators followed by discontinuous multi-stage crystallization (cooking). Only one process to carry out juice purification has been considered (sulfitation, liming, heating, sedimentation, and filtering), although there are two ways to concentrate the clarified juice to produce sugar. The first technology yields white sugar, raw sugar, and molasses (technology T1), while the second one produces white sugar, raw sugar, and a secondary honey (technology T2). These two by-products differ in their sucrose content. Molasses is a viscous dark honey whose low sucrose content cannot be recovered by crystallization, while secondary honey is a liquid with a higher amount of sucrose that leaves the sugar mill before being exhausted by crystallization. White sugar has been taken as the main product for both technologies in this subsystem. Allocation between sugars and molasses in T1 and sugars and honey in T2 has been done in a mass basis. Table 3 shows the results for the inventory phase of the subsystem sugar production.

In the subsystem *Ethanol Production*, a yeast-prepared substrate is inoculated (*Saccharomyces cerevisiae*), which converts saccharose ($C_{12}H_{22}O_{11}$) and other fermentable carbohydrates into ethanol and CO_2. The process takes place in open discontinuous fermentation tanks. According to the most common practice in Tucumán, the fermented product is transported to a train of three distillation columns to obtain the desired alcohol concentration. The products of distillation are hydrated alcohol 97 °GL, low-grade ethanol, and fusel oil. Three different technologies can

Table 1 Summary of the yearly inventory data for the subsystem *Agriculture* (reference flow, 1 kg sugarcane harvested)

	Value	Unit	Comments
Inputs			
Land use (Perez et al. 2007)	1.49E−05	ha	
Urea[a]	2.99E−03	kg	Urea, as N, at regional storehouse
Superphosphate[a]	3.58E−04	kg	Triple superphosphate, as P_2O_5, at regional storehouse
Pesticides[a]	2.69E−04	kg	Nitro compounds, at regional storehouse
Filter muds[a]	4.00E−02	kg	3.5 kg filter mud/100 kg cane; it contains colloidal organic matter, 15–30 % of fiber, 5–15 % proteins, 5–15 % crude wax and fats, 10–20 % ash including oxides of Si, Ca, Mg, and K
Fuel oil (EcoInvent Database 2009)	1.78E−03	kg	Diesel, at regional storage
Outputs			
Ash[a]	5.67E−03	kg	Avoided credit: disposal, wood ash mixture, pure, 0 % water, to land farming
Emissions air[b] (Renouf et al. 2008)	1.00E−03	kg	7.76E−02 kg NH_3, −6.27E−02 kg CO_2, 2.17E+01 kg CO, 2.00 E−01 kg N_2O, 1.02E+00 kg NO_x, 6.20E−02 kg SO_x, 1.50E+01 kg particulates >10 μm
Emissions water[b] (Renouf et al. 2008)	1.00E−03	kg	1.94E−01 kg NO_3^-, 3.82E−01 kg PO_4^{3-}
Sugarcane harvested	1	kg	

[a] Technical Reports on the Sugar Cane Industry, Universidad Nacional de Tucumán, 2010

[b] Obtained through carbon balance calculations (photosynthesis+respiration+combustion)

Table 2 Summary of the yearly inventory data for the subsystem *Milling* (reference flow, 1 kg sugarcane juice)

	Value	Unit	Comments
Inputs			
Sugarcane harvested	1.11E+00	kg	
Water	4.54E−01	kg	Tap water, at user
Outputs			
Avoided electricity 132.1 MJ[a]	4.09E−02	kWh	The subsystem produces 132.1 MJ for export to the network; electricity mix in Argentina[b]
Avoided electricity 54.0 MJ[a]	1.67E−02	kWh	The subsystem produces 54 MJ used in the process operation; electricity mix in Argentina[b]
Avoided steam 0.504 t[a]	5.61E−01	kg	The subsystem produces 0.504 t used in the process operation
Avoided bagasse 0.02 t[a]	2.23E−02	kg	The subsystem produces 0.02 t used in the process operation; bagasse, from sugarcane, at sugar refinery
Emissions air (US Environmental Protection Agency 1996)	1.11E−03	kg	2.58E+02 kg CO_2, 2.00E−01 kg NO_x, 1.00E−01 kg SO_2, 2.00E−01 kg particulates >10 μm
Emissions water (US Environmental Protection Agency 1996)	1.11E−03	kg	1.90E+00 kg dissolved solids
Sugarcane juice	1	kg	

[a] Technical Reports on the Sugar Cane Industry, Universidad Nacional de Tucumán, 2010

[b] Secretaría de Energía de la Nación (2009)

be distinguished, depending on the raw material arriving to the distillery: molasses (technology T3), secondary honey (technology T4), or sugarcane juice (technology T5). All three technologies consume the same inputs (e.g., water, yeasts, etc.), but the consumption rates differ in each case. These technologies lead in turn to different

Table 3 Summary of the inventory data for sugar production to molasses (T1) and honey (T2) (reference flow, 1 kg molasses or honey)

	Value T1	Value T2	Unit	Comments
Inputs				
Sugarcane juice	4.13E+00	4.13E+00	kg	
Steam[a]	2.04E+00	1.71E+00	kg	Steam, for chemical processes, at plant
Lime[a]	9.32E−03	9.20E−03	kg	Lime, algae, at regional storehouse
Sulphur[a]	1.40E−03	1.38E−03	kg	Sulfuric acid, liquid, at plant
Oxygen[a]	2.52E−03	2.48E−03	kg	Oxygen, liquid, at plant
Flocculant (Renouf et al. 2008)	5.59E−07	5.52E−07	kg	Iron (III) chloride, 40 % in H_2O, at plant
NaOH[a]	7.82E−04	7.36E−04	kg	Sodium hydroxide, 50 % in H_2O, production mix, at plant
HCl[a]	1.51E−03	1.47E−03	kg	Hydrochloric acid, 30 % in H_2O, at plant
Outputs				
Emissions air (Renouf et al. 2008)	5.59E−04	4.60E−04	kg	T1, 5.00E−01 kg SO_2; T2, 6.00E−01 kg SO_2
Emissions water (Renouf et al. 2008)	5.59E−04	4.60E−04	kg	T1, 2.10E−03 kg BODs, 6.96E+01 kg dissolved solids, 3.20E−03 kg suspended solids; T2, 6.00E−01 kg SO_2, 2.60E−03 kg BODs, 8.35E+01 kg dissolved solids, 3.90E−03 kg suspended solids
Filters muds (Hugot 1986)	8.09E−01	5.33E−01	kg	Avoided credit, 3.5 % of filter mud (contains colloidal organic matter, 15–30 % of fiber, 5–15 % proteins, 5–15 % crude wax and fats, 10–20 % ash including oxides of Si, Ca, Mg, and K) per weight of cane
Sugars[a]	6.57E−01	5.43E−01	kg	T1, 1,000 kg white sugar and 176 kg raw sugar; T2, 1,000 kg white sugar and 180 kg raw sugar
Molasses (T1) or honey (T2)	1	1	kg	

[a] Technical Reports on the Sugar Cane Industry, Universidad Nacional de Tucumán, 2010

amounts of nearly the same emissions (i.e., CO_2, VOCs, fuel oil, etc.). The hydrated ethanol, which is close to its azeotropic composition, is dehydrated through molecular sieves. Each of the three technologies generates a harmful liquid residue called vinasses in a ratio of 15 L vinasse/L ethanol produced. Vinasse properties depend on the raw material used in the process. Currently, each ethanol company in Argentina implements a different waste disposal option. In this study, we have considered an average impact for disposing vinasses in soil and surface watercourses. Table 4 shows the results for the inventory phase of the subsystem *Ethanol Production*. Moreover, only technologies T1+T3 are applied in Argentina, but technologies T2+T4 and T5 are promising candidates due to the increasing demand of ethanol and the good performance of these technologies in other countries, e.g., Brazil. Previous works of the authors also consider these options (Mele et al. 2011).

Steam generation and use deserve a special digression. In the subsystem *Milling*, the bagasse obtained from sugarcane juice extraction is burnt in boilers to produce steam in a closed loop to cover both power and heating needs of the sugar plants and distilleries. Moreover, electricity is produced by steam-driven generators. In this study, for pathways 1 and 2, we considered that all the steam generated is consumed by the sugar plant and distillery, and extra steam is considered to enter distilleries in order to cover its needs. However, in the case of pathway 3, distillery T5 does not consume all the steam produced, and therefore, there is a steam surplus that is considered as a coproduct, since it can be used in other processes out of the system boundaries. In this case, its environmental impacts have been avoided by including the steam production process within the system boundaries.

Regarding CO_2, the worst case has been taken; that is, the complete mass balance of CO_2, taking all the CO_2 inputs and outputs, has been considered, using the impact factors corresponding to fossil CO_2. The "Electronic supplementary material" shows the detailed LCI and LCIA for each subsystem addressed here.

Table 4 Summary of the yearly inventory data for ethanol production from molasses distillery (T3), honey distillery (T4), and cane juice distillery (T5) (reference flow, 1 kg ethanol)

	Value T3	Value T4	Value T5	Unit	Comments
Inputs					
Molasses (T3), honey (T4), or sugarcane juice (T5)	4.00E+00	3.35E+00	1.19E+01	kg	
Steam	3.85E+00	2.97E+00	4.99E+00	kg	Steam, for chemical processes, at plant
Urea	4.26E−03	4.26E−03	4.26E−03	kg	Urea, as N, at regional storehouse
H_3PO_4	3.55E−04	3.55E−04	3.55E−04	kg	Phosphoric acid plant, fertilizer grade
Water	1.63E−03	1.63E−03	1.63E−03	kg	Tap water, at user
H_2SO_4	1.15E−02	1.15E−05	1.15E−05	kg	Sulfuric acid, liquid, at plant
Outputs					
Emissions air (Cortez et al. 1997)	8.88E−04	8.88E−04	8.88E−04	kg	T3, 3.37E+03 kg CO_2; T4, 3.37E+03 kg CO_2; T5, 3.37E+03 kg CO_2
Emissions water (Cortez et al. 1997)	8.88E−04	8.88E−04	8.88E−04	kg	T3, 1.45E+03 kg COD, 5.28E+02 kg DBO_5, 1.58E+03 kg total solids, 5.65 E+02 kg, 2.97E+01 kg Ca, 6.4E+00 kg Mg, 7.8E+00 kg Na, 1.95E+02 kg K, 2.19E+01 kg N, 1.6E+00 kg P
					T4, 1.45E+03 kg COD, 5.28E+02 kg DBO_5, 1.58E+03 kg total solids, 5.65 E+02 kg, 2.97E+01 kg Ca, 6.4E+00 kg Mg, 7.8E+00 kg Na, 1.95E+02 kg K, 2.19E+01 kg N, 1.6E+00 kg P
					T5, 1.45E+03 kg COD, 5.28E+02 kg DBO_5, 2.21E+02 kg total solids, 4.35 E+02 kg inorganic solids, 1.69E+01 kg Ca, 3.2E+00 kg Mg, 2.7E+00 kg Na, 6.82E+01 kg K, 5.5E+00 kg N, 1.1E+00 kg P
Ethanol LG	1.11E−01	1.11E−01	1.11E−01	kg	
Fuel oil	1.51E−03	1.51E−03	1.51E−03	kg	
Steam excess			1.69E+00	kg	Steam excess produced in T5 which is used as feedback
Ethanol	1.00	1.00	1.00	kg	

3 Results and discussion

3.1 Life cycle impact assessment of the reference case

For the RC, the eight impact categories considered in the LCIA phase of the study are AP (global, kilograms SO_2 equivalent), GWP (kilograms CO_2 equivalent), EP (global, kilograms PO_4 equivalent), PHO (kilograms ethylene equivalent), DAR (kilograms Sb equivalent), ODP (kilograms CFC-11 equivalent), FWAET (kilograms 1,4-DCB equivalent), and TET (kilograms 1,4-DCB equivalent). All the impact values for each subsystem (agriculture, milling, sugar production, and ethanol production) are shown in Table 5. The impacts are referred to 1 kg of ethanol as the FU. From Table 5, it can be deduced that P1 has the highest impact, except for AP, followed by P2, and finally P3, which is the most environmentally convenient path.

3.1.1 Global warming potential

Agriculture is the unit process that most contributes to GWP with 13.3 kg CO_2 in pathway 1 (59.0 %), 11.1 kg CO_2 in pathway 2 (57.9 %), and 9.54 kg CO_2 in pathway 3 (63.6 %) mainly due to the fossil fuel consumption in trucks and machines used in cultivation, harvesting, and transportation activities (Fig. 4). Ethanol production by distillery T4 has 19.3 % of the total impact in pathway 2 because of the emissions of 3.7 kg CO_2 to the air during fermentation. Similar impacts are obtained for T3, being 3.91 kg CO_2 (17.4 %), as they have similar processes. T5 has lower impact than the ones before with 2.61 kg CO_2 because this technology shows an avoided impact charge due to the excess steam production from the subsystem *Milling*.

Pathway 1 shows the highest impact with 22.5 kg CO_2 compared to pathways 2 and 3 with 19.2 and 15.0 kg CO_2, respectively. This difference of the three pathways lies in the conversion factors in the subsystem *Agriculture*, which is higher in pathway 1, to produce 1 kg of ethanol, taking into account the 0.72 kg CO_2/kg sugarcane harvested. Pathways 1 and 2 exhibit similar values of impact because the results for the subsystem *Sugar Production* are quite similar using either technology T1 or technology T2.

Table 5 Impact categories in different subsystems to produce ethanol for each pathway (FU=1 kg of ethanol)

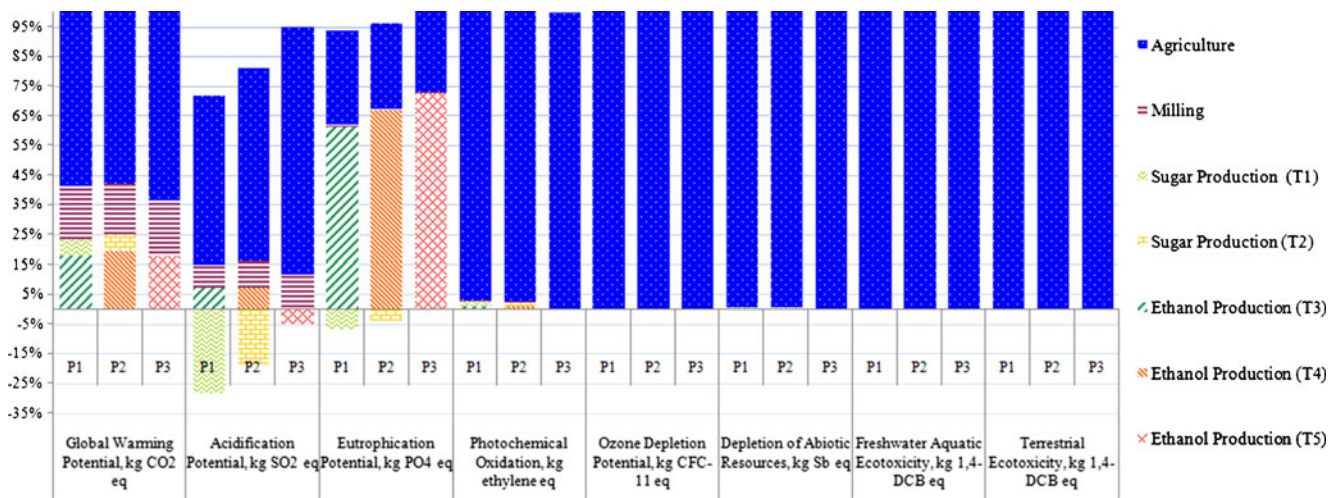|	Pathways	Subsystem 1: agriculture	Subsystem 2: milling	Subsystem 3: sugar production		Subsystem 4: ethanol production			Total
				T1	T2	T3	T4	T5	
GWP, kg CO_2 eq	P1	1.33E+01	3.95E+00	1.36E+00	–	3.91E+00	–	–	2.25E+01
	P2	1.11E+01	3.31E+00	–	1.05E+00	–	3.70E+00	–	1.92E+01
	P3	9.54E+00	2.84E+00	–	–	–	–	2.61E+00	1.50E+01
AP, kg SO_2 eq	P1	1.93E−02	2.67E−03	−9.70E−03	–	2.39E−03	–	–	1.46E−02
	P2	1.61E−02	2.23E−03	–	−4.72E−03	–	1.72E−03	–	1.54E−02
	P3	1.39E−02	1.92E−03	–	–	–	–	−8.78E−04	1.49E−02
EP, kg PO_4 eq	P1	2.12E−02	3.27E−04	−4.49E−03	–	4.11E−02	–	–	5.82E−02
	P2	1.78E−02	2.73E−04	–	−2.40E−03	–	4.10E−02	–	5.67E−02
	P3	1.53E−02	2.35E−04	–	–	–	–	4.08E−02	5.63E−02
PHO, kg ethylene eq	P1	1.35E−02	3.22E−05	2.70E−04	–	1.25E−04	–	–	1.39E−02
	P2	1.13E−02	2.69E−05	–	1.84E−04	–	9.14E−05	–	1.16E−02
	P3	9.70E−03	2.31E−05	–	–	–	–	−4.80E−05	9.68E−03
ODP, kg CFC-11 eq	P1	3.82E−03	−5.09E−08	3.39E−07	–	1.77E−07	–	–	3.82E−03
	P2	3.19E−03	−4.26E−08	–	2.47E−07	–	1.37E−07	–	3.19E−03
	P3	2.74E−03	−3.66E−08	–	–	–	–	−7.35E−08	2.74E−03
DAR, kg Sb eq	P1	4.12E+00	−2.15E−03	1.34E−02	–	7.37E−03	–	–	4.14E+00
	P2	3.44E+00	−1.80E−03	–	9.78E−03	–	5.72E−03	–	3.46E+00
	P3	2.96E+00	−1.55E−03	–	–	–	–	−3.05E−03	2.96E+00
FWAET, kg 1,4-DCB eq	P1	2.60E+02	−9.14E−03	−2.30E−02	–	2.88E−02	–	–	2.60E+02
	P2	2.17E+02	−7.64E−03	–	−1.25E−03	–	2.23E−02	–	2.17E+02
	P3	1.87E+02	−6.57E−03	–	–	–	–	−9.05E−03	1.87E+02
TET, kg 1,4-DCB eq	P1	8.11E+01	−2.43E−03	−9.37E−03	–	5.04E−03	–	–	8.11E+01
	P2	6.78E+01	−2.03E−03	–	−3.5E−03	–	3.91E−03	–	6.78E+01
	P3	5.83E+01	−1.75E−03	–	–	–	–	−2.07E−03	5.83E+01

Fig. 4 Relative contribution of environmental impact categories for each pathway

3.1.2 Acidification potential

The subsystem *Agriculture* becomes the most important contributor in this impact category with 1.93E−02, 1.61E−02, and 1.39E−02 kg SO$_2$ equivalent (see Table 5), with a relative contribution of 131.7, 105, and 93.0 % for each pathway (see Fig. 4) of the total impact in this category. It can be attributed to the NO$_x$ emitted during cane burning and fossil fuel combustion and also to the manufacturing and decomposition in the soil of fertilizers. Distilleries T3 and T4 have also high impact values around 16.4 and 11.2 %, respectively, due to the combustion of fossil fuels during steam generation, whereas T1 and T2 show avoided amounts of SO$_2$ due to the use of the filter muds as raw material for other process. Also, T5 shows avoided credits due to the excess of steam coming from the subsystem *Milling*.

3.1.3 Eutrophication potential

Overall, the three distilleries (T3, T4, and T5) have the most important impact in this indicator, with 4.11E−02, 4.10E−02, and 4.08E−02 kg PO$_4$ (see Table 5) equivalent with 70.6, 72.3, and 72.5 % (see Fig. 4) in each technology, respectively. It is due to the emission of a high volume of vinasses to the watercourses with high content of chemical oxygen demand (COD), nitrogen, and phosphorus. This indicator shows also some negative values due to the avoided impact charges of reusing filter muds in T1 and T2.

3.1.4 Photochemical oxidation

Agriculture is the subsystem that shows the highest impact in this category, with 1.35E−02 and 1.13E−02 kg ethylene for pathways 1 and 2, respectively; impact in pathway 3 is 9.70E−03 kg ethylene (see Table 5) due to the emission of carbon monoxide and sulfur dioxide to air when the fossil

fuel and the sugarcane are burned. Hence, the subsystem *Agriculture* shows, in three pathways, approximately 96–100 % of the total impact.

Almost 100 % of the impact in categories such as *ODP*, *DAR*, *FWAET*, and *TET* can be attributed to the subsystem *Agriculture* because of the use of pesticides, which contain methane and halocarbon compounds. This value can be adjusted accurately, provided that the pesticides composition is known. Water consumption due to artificial irrigation in the aforementioned subsystem is not an issue, unlike the case, for instance, of Brazil (Faist et al. 2011).

In addition, we assessed the land use indicator which has only been considered in the *Agriculture* subsystem. The LCI provides the land use impact, which is 2.74E−04, 2.30E−04, and 1.97E−04 ha for pathways 1, 2, and 3, respectively.

3.2 Sensitivity analysis

Figure 4 shows the relative contribution of each impact category at each subsystem. Because of the relatively high contribution of GWP, a detailed assessment for this category impact is developed upon the RC. Related to that, under Law 26.190 of 2006 and its regulatory framework, the Argentinean Government created the program Genren (Renewable Generation). Its main objective is to reduce emissions of CO$_2$ and other GHG. In addition, Argentina, in early 2010, joined the Global Research Alliance, established to increase international cooperation, collaboration, and investment to help reduce the GHG emissions of agricultural production and increase its potential for soil carbon sequestration (Joseph 2010).

A sensitivity analysis to study the variability of the GWP according to different criteria has been performed. Case study 1 considers changes in the agricultural yield; case

study 2 includes the economic allocation in the subsystem *Sugar Production* (technologies T1 and T2); case study 3 takes into account the effect of changes in the sugar price; and finally, case study 4 shows the effect of using energy-based allocation in the subsystem *Sugar Production* (technologies T1 and T2).

3.2.1 Variation in the agricultural yield (case study 1)

The agricultural yield regarded in the subsystem *Agriculture* is an important source of exogenous uncertainty, which strongly depends on weather conditions. The system considered so far is called the RC, and three additional scenarios have been studied. The objective is to know the behavior of the GWP when agricultural yield increases 10 % and decreases 10 % from the RC value. Therefore, the yield values considered in the three scenarios are 73.7 t/ha (scenario 1, +10 %), 67 t/ha (scenario 2, RC), and 60.3 t/ha (scenario 3, −10 %). Note that, on agricultural yield variations, some inputs and outputs from the reference inventory are modified. For example, the consumption of fuel oil, urea, superphosphate, and pesticides changes. The same occurs with the emissions to the water (pesticides, PO_4^{3-}, and NO_3^-) and to the air (NO_x, N_2O, and NH_3).

As expected, results indicate that, in all pathways, when the yield decreases in the subsystem *Agriculture*, the GWP impact raises and, when the yield increases, the GWP impact does the opposite. Comparing the three pathways shown in Table 6, it is possible to identify, in pathway 1, that, at 60.3 t/ha yield (10 % below RC value), the total impact of 25.3 kg CO_2 is the highest due to the huge impact in the subsystem *Agriculture*. It is interesting to take into account that the relative contribution from the RC is plus 12.3 %, whereas we only have decreased 10 % of the yield, given that there is no direct relation of percentage. On the other hand, the least harmful scenario for the environment is scenario 1 (maximum yield), shown in pathway 3 with 13.1 kg CO_2.

3.2.2 Economic allocation in the subsystem Sugar Production using technologies T1 and T2 (case study 2)

The objective of this subsection is to quantify the total GWP changes when economic allocation is considered in the subsystem *Sugar Production*, using either T1 or T2 (scenario 1), instead of using mass allocation as in the RC (scenario 2). The economic allocation has been calculated after reviewing the sugar and ethanol prices from Centro Azucarero Argentino (2010) and the Ministerio de Planificación Federal, Inversión Pública y Servicios (2010), respectively. These amounts have been converted into dollars for the study (exchange rate of October 2010).

Table 7 shows that, through pathways 1 and 2, the total GWP impact with economic allocation is lower than this impact with mass allocation (RC). This is because ethanol is relatively cheaper than sugars; thus, ethanol production carries a lower amount of environmental burden. It is interesting to remark that changes are higher in pathway 1 (from scenario 1 to 2 is 10.7 kg CO_2) than in pathway 2 (from scenario 1 to 2 is 7.1 kg CO_2). Hence, results point out the importance of selecting the allocation for each study due to the different sensitivities of the process studied. This had been already brought up in previous works on ethanol LCA (García et al. 2011; Ometto et al. 2009).

To sum up, from the environmental point of view, scenario 1 (economic allocation) in pathway 1 (Agriculture+Milling+Sugar Production-T1+Ethanol Production-T3) is the best suitable scenario to produce ethanol with 11.8 kg CO_2 of total impact, with scenario 2 in that pathway (mass allocation) being the worst one with 22.5 kg CO_2.

3.2.3 Variation in the sugar price (case study 3)

As the ethanol price is fixed by the Argentinean Government and the sugar price changes according to the international market, the objective of this case study is to see how the total GWP is affected if the sugar price increases or decreases 10 % from the RC.

Table 6 GWP (kilograms CO_2 equivalent) for the three pathways, in case study 1 (FU=1 kg ethanol)

	Pathway 1			Pathway 2			Pathway 3		
	Scenario 1	Scenario 2	Scenario 3	Scenario 1	Scenario 2	Scenario 3	Scenario 1	Scenario 2	Scenario 3
Agriculture	10.7	13.3	16.0	8.95	11.1	13.4	7.69	9.54	11.5
Milling	3.95	3.95	3.95	3.31	3.31	3.31	2.84	2.84	2.84
T1—sugar production to molasses	1.36	1.36	1.36				–	–	–
T2—sugar Production to honey	–	–	–	1.05	1.05	1.05			
T3—distillery to ethanol (molasses)	3.91	3.91	3.91	–	–	–	–	–	–
T4—distillery to ethanol (honey)	–	–	–	3.70	3.70	3.70	–	–	–
T5—distillery to ethanol (cane juice)	–	–	–	–	–	–	2.61	2.61	2.61
Total	19.9	22.5	25.3	17.0	19.2	21.5	13.1	15.0	17.0
Change relative to the RC, %	−11.4	0.0	12.3	−11.2	0.0	12.1	−12.3	0.0	13.3

Table 7 GWP (kilograms CO_2) in pathways 1 and 2, considering economic allocation versus mass allocation in subsystem sugar production

	Pathway 1		Pathway 2	
	Scenario 1	Scenario 2	Scenario 1	Scenario 2
Agriculture	5.76	13.3	6.16	11.1
Milling	1.72	3.95	1.84	3.31
T1—sugar production to molasses	0.266	1.36	–	–
T2—sugar production to honey	–	–	0.442	1.05
T3—distillery to ethanol (molasses)	4.06	3.91	–	–
T4—distillery to ethanol (honey)	–	–	3.91	3.70
Total	11.8	22.5	12.1	19.2
Change relative to the RC (%)	−47.5	–	−35.5	–

This case study works with pathways 1 and 2, given that only these pathways produce sugar through technologies T1 and T2, respectively. This case study is based on modifying the price of sugar used in case study 2, i.e., modifying the economic allocation factors.

Scenario 2 in both pathways considers the RC with economic allocation. Hence, scenario 1 corresponds to an increase of 10 % on the sugar price, while scenario 3 represents a decrease of 10 %.

Table 8 shows that, when the sugar price decreases, total GWP also increases, since the ethanol allocation factor turns to be higher than the sugar factor.

Finally, comparing scenarios 1 and 3, some conclusions about changes in the GWP impact corresponding to changes in the sugar price can be derived. By and large, the tendency in both pathways is as follows: When the reference price of sugar increases 10 %, the total GWP impact slightly decreases, whereas if the sugar price is reduced by10 %, the impact also increased, but in a higher percentage.

Regarding the results from Table 8, the most favorable scenario to produce ethanol is through pathway 1 (Agriculture + Milling + Sugar Production-T1 + Ethanol Production-T3), using economic allocation with 10 % high prices for sugar. This scenario impacts with 11.1 kg CO_2. On the other hand, the worst case is though pathway 2 (Agriculture + Milling + Sugar Production-T2 + Ethanol

Production-T4), using economic allocation with 10 % less prices for sugars in scenario 3 (13.1 kg CO_2).

3.2.4 Calorific value allocation in the subsystem Sugar Production using technologies T1 and T2 (case study 4)

The objective of this subsection is to quantify the total GWP changes when calorific allocation is considered in the subsystem *Sugar Production*, using either T1 or T2 (scenario 1), instead of using mass allocation as in the RC (scenario 2). Even though sugar is not an energy product (i.e., not used as a fuel), it is interesting to complete the allocation analysis with some conclusions related to the energy content of the products, with the work of García et al. (2011) being an antecedent. The calorific allocation has been calculated after reviewing the sugar (Food Database (FDDB) 2012) and ethanol (Edwards et al. 2011) calorific values. If we compare the total GWP values obtained from calorific allocation (scenario 1) with the mass allocation (RC) (scenario 2), Table 9 provides lower impacts for scenario 1. Pathway 1 in scenario 1 is reduced from scenario 2 by 40.3 % and pathway 2 is reduced by 27.9 %. This is because ethanol's calorific value is relatively higher than sugars. Likewise, this case study shows again the importance of choosing a suitable allocation. Analogously to Section 3.2.2, the best scenario to produce ethanol at the environmental impact point of view is scenario

Table 8 GWP (kilograms CO_2) in pathways 1 and 2, taking into account economic allocation in the RC versus economic allocation with modified sugar price ±10 %

	Pathway 1			Pathway 2		
	Scenario 1	Scenario 2	Scenario 3	Scenario 1	Scenario 2	Scenario 3
Agriculture	5.29	5.76	6.33	5.72	6.16	6.69
Milling	1.58	1.72	1.89	1.70	1.84	1.99
T1—sugar production to molasses	0.198	0.266	0.348	–	–	–
T2—sugar production to honey	–	–	–	0.387	0.442	0.507
T3—distillery to ethanol (molasses)	4.07	4.06	4.05	–	–	–
T4—distillery to ethanol (honey)	–	–	–	3.93	3.70	3.89
Total	11.1	11.8	12.6	11.7	12.1	13,1
Change relative to the RC, %	−5.63	–	6.81	−3.34	–	7.71

Table 9 GWP (kilograms CO$_2$) in pathways 1 and 2, considering calorific value allocation versus mass allocation in subsystem sugar production

	Pathway 1		Pathway 2	
	Scenario 1	Scenario 2	Scenario 1	Scenario 2
Agriculture	6.90	13.3	7.22	11.1
Milling	2.06	3.95	2.15	3.31
T1—sugar production to molasses	0.432	1.36	–	–
T2—sugar production to honey	–	–	0.571	1.05
T3—distillery to ethanol (molasses)	4.04	3.91	–	–
T4—distillery to ethanol (honey)	–	–	3.87	3.70
Total	13.4	22.5	13.8	19.2
Change relative to the RC (%)	−40.3	–	−27.9	–

1 (calorific allocation) in pathway 1 (Agriculture+Milling+ Sugar Production-T1+Ethanol Production-T3).

4 Conclusions

Law 26.093 in Argentina is an opportunity for bioethanol production to use and mobilize human and natural resources. Argentinean bioethanol producers will need to study the environmental performance of their product in order to comply with the sustainability criteria because the LCIA concludes that the ethanol life cycle contributes to all the impacts analyzed. The sugarcane industry does not only affect the environment in terms of global warming but it also contributes to other impacts like acidification and eutrophication (Chauhan et al. 2011).

The RC study to produce 1 kg of ethanol shows that (1) pathway 1 emits 22.5 kg CO$_2$, of which relative contributions are structured as S1—agriculture (59.0 %), S2—milling (17.6 %), S3—sugar production T1 (6.00 %), and S4—distillery T3 (17.4 %); (2) pathway 2 emits 19.2 kg CO$_2$, with a relative contribution of the main impacts S1—agriculture (57.9 %), S2—milling (17.3 %), S3—sugar production T2 (5.50 %), and S4—distillery T4 (19.3 %); and (3) pathway 3 emits 15.0 kg CO$_2$, of which relative contributions are S1—agriculture (63.6 %), S2—milling (19.0 %), and S5—distillery T5 (17.4 %). Generally, all pathways have similar relative distributions, with the subsystem *Agriculture* having the highest impact. This conclusion is reinforced by LCA studies conducted in other countries (García et al. 2011; Pereira and Ortega 2010; Ometto et al. 2009). However, pathways 1 and 2 have similar impacts because they have similar technologies, with both pathways having a higher impact than pathway 3. Hence, the influence of the cane processing system and agricultural yield variability suggests that studies should be specific, concentrating at the regional scope. The recommendations that can be drawn are strongly related with those set by other authors in other countries (Nguyen and Gheewala 2008; Ometto et al. 2009): (1) substituting fossil for biomass-based fuels in agriculture labor; (2) wastewater treatment at distilleries; (3) using cane trash for

energy instead of open burning in fields; and (4) water recycling systems during industrial processing.

The sensitivity analysis allows drawing conclusions in three respects: (1) As the subsystem *Agriculture* includes the sections with a higher contribution to the environmental impact of ethanol production, this impact is strongly influenced by agricultural yields; (2) the LCA results for the Argentinean bioethanol are strongly dependent of the process pathway selected; (3) the environmental impact calculated on a financial allocation basis can mask the impact of bioethanol production as it becomes dependent on the relative market price of sugar/ethanol.

Impact allocation to the multiple products system from sugarcane is an important issue (García et al. 2011; Renouf et al. 2011). When coproducts appear (e.g., molasses, electricity, ethanol), economic allocation is less useful due to uncertainty in the mechanism for assigning impacts. To enable the consistent representation of impact across the full range of sugarcane products, mass allocation combined with energy allocation for the energy obtained from bagasse combustion and cogeneration is preferable.

Although, so far, the uncertainty associated with Argentinean ethanol production is very high, the consideration of the water treatment subsystem within the system boundaries of the study is an issue of enormous importance that should be considered in future works.

According to the large amount of variables and process options that participate in the environmental evaluation of products like bioethanol, the results presented in this paper demonstrate the need for progress in the standardization of protocols to calculate impacts based on the LCA of products. The international market of products considered as commodities requires common frames to evaluate the sustainability of products addressed to the final consumer.

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