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Review

Sustainability of the Biorefinery Industry for Fuel Production

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Abstract: Biofuels have been extensively explored and applied in the Brazilian market. In Brazil, ethanol and biodiesel are produced on an industrial scale. Ethanol is commercialized and used in engines in both the hydrated form (96% °GL) and the anhydrous form, mixed with gasoline at a proportion of up to 25% by volume. In turn, biodiesel is blended with diesel in a proportion of 5% by volume. Thus, the goal of the use of biofuels is to contribute to the mitigation of greenhouse gases and other pollutants emitted into the atmosphere during burning. This article describes some recent developments in the characterization of the environmental and economic impacts of the production of these biofuels from different biomass sources. On this regard, this review presents results of life-cycle assessments (LCAs), life-cycle cost assessments (LCCAs) and Structural Path Analysis (SPA), this last one depicting a sectorial perspective rather than LCA process level data approaches. The results showed that the inclusion of biofuels in transportation activities can lead to the mitigation of the environmental impacts of certain activities, such as emissions of greenhouse gases. However, greater attention must be paid to the improvement of agricultural management to decrease fuel, fertilizer and herbicide consumption.

Keywords: biorefinary; bio-oils; biodiesel; bioethanol; first- and second-generation ethanol; LCA

1. Introduction

There are numerous environmental problems caused by the intensive use of fossil fuels (e.g., carbon dioxide [CO_2] emissions, pollution and resource depletion), which highlights the disadvantages of an unbalanced ratio of resource demands associated with this non-renewability. The growing interest in alternative renewable resources, such as CO_2-neutralizing materials, suggests that biomass derived from agricultural products is an important source of raw materials for various products and biofuels [1,2].

Regarding biomass use, life-cycle assessments (LCAs) can be applied to determine the environmental impacts of the production of a product, such as soybean oil, palm oil, sugarcane, biodiesel and ethanol while simultaneously integrating various environmental aspects, known as environmental impact categories, into the assessment. These categories include global warming [3], atmospheric acidification, eutrophication and human toxicity [4], among others. Moreover, this methodology has been applied to assess up to the third generation biofuels [5–7].

Coupled with LCA, life-cycle cost assessment (LCCA) is a method that determines the costs associated with supply-chain assets, such as the costs of acquisition, installation, operation, inputs, maintenance, recycling and disposal. This type of model is static; therefore, it cannot be used to model market dynamics because it considers only production costs [8].

Brazil biofuel production, one of the largest in the world, was of 29 billion liters of ethanol in 2009 and of 2.4 billion liters of biodiesel in 2010 [2]. This production will increase in the next years as the fleet grows and the biodiesel diesel ration augments to 10% [2].

This article will discuss some results of recent studies on the environmental and economic impacts of biodiesel and ethanol production in the Brazilian context. The research focused on primary and secondary data of first and second-generation sugarcane bioethanol and biodiesel from several oleaginous.

2. Bio-oils

Biodiesel has been established as a successful fuel in the Brazilian energy matrix, and Brazil is nowadays the third greatest producer worldwide [9]. Biodiesel can be produced from a wide variety of oleaginous plants, such as soybean, cotton, babassu and palm. Several aspects of soybean oil and palm oil production will be discussed below, and a description of biodiesel production via oil treatment and transesterification will be presented, as will a comparative evaluation of the environmental impacts along the biodiesel life-cycle. In order to protect intellectual property of data owners, suppliers' names and mass and energy flows figures are confidential.

2.1. Soybean

Soybean (*Glycine max* L.) is one of the most important crops in the World, due to its oil and protein content [10]. Global soybean production is approximately 210 million tons per year. The main countries producing this crop are the U.S. (39.4% of global production), Brazil (23.9%) and Argentina (18.2%) [11]. In Brazil, soybeans are intended to be consumed "in natura" or processed, in the form of soybean meal (used in the manufacture of animal feed) and soybean oil (used in food or in the production of biodiesel).

The global cultivation area for soybean increased from 38 million hectares (ha) in 1975 to 91 million ha in 2005, with the most significant increases occurring in Argentina and Brazil [12]. Brazil is the second-largest soybean producer in the World, generating approximately 67 million tons on 25 million ha, with a productivity of 2665 kg/ha [13]. Soybean oil represents 85% of Brazilian biodiesel production.

The Brazilian agricultural model is sustainable and competitive, pioneering the support of programs to reduce greenhouse gas emissions, such as low-carbon agriculture [14]. The total cultivated area in Brazil is estimated at 49.9 million ha [15]. Agricultural expansion mainly occurs in parts of the Cerrado, and the resulting impacts have stimulated discussions about good agricultural practices to promote increased productivity, prevent deforestation and reduce the emissions related to the advancement of soybean cultivation [13].

Soy is the crop that consumes the greatest amount of agricultural inputs (45.3%) in Brazil [16]. Due to the environmental consequences of the accumulation and dispersion of these agrochemicals, LCAs of agricultural products have become a tool for implementing the concept of sustainable development to ensure the profitability of farms and the conservation of natural resources [17].

The amount of inputs influences environmental impact categories, even when analyzed independently of other agricultural processes. The agricultural data available in literature demonstrates that the contributions of herbicides and pesticides to eutrophication and toxicity can be partly explained by the behavior of these agrochemicals in soil and by the processes involved in their production [17]. With respect to fertilizers, phosphate use produces the greatest environmental impact, especially in terms of the CO_2-equivalent emissions associated with the production process and the ease of adsorption to soil elements, which increase emissions in the other categories. Xavier [17] also noted that in agriculture, more intensive use of fertilizer does not translate into higher productivity but does produce greater environmental impacts without achieving better economic results.

2.2. Palm Oil

Although it does not yet represent a large share of biodiesel production (contributing approximately 0.25%), the palm, or dendê (*Elaeis guineensis*), shows great potential, especially in the northern region of Brazil [18]. The average yield of crude palm oil ranges from 3 to 6 tons per ha, compared to the soybean yield of 0.2 to 0.6 tons per ha [19]. Some additional benefits of palm oil are that it is a perennial crop and is well adapted to the edaphoclimatic conditions of the Amazon region [20].

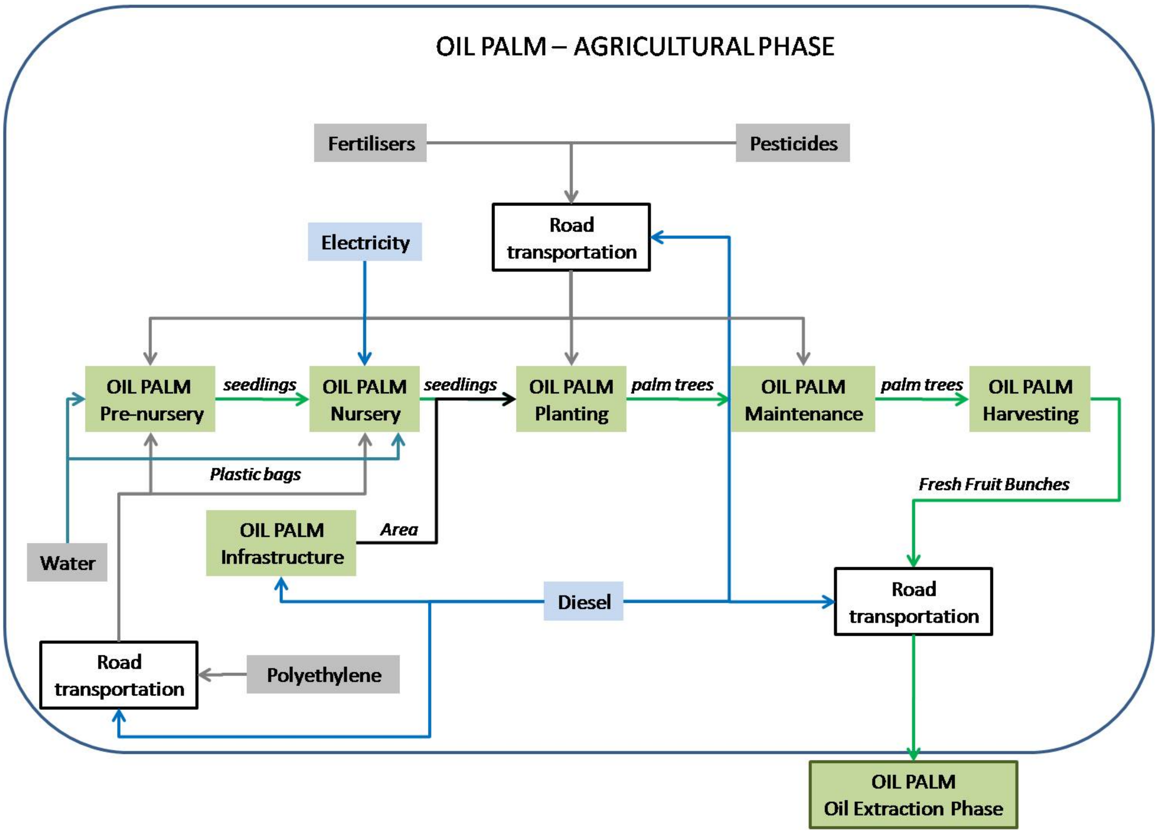
The technological system analyzed below is the idealization of a potential system based on secondary data available in the technical-scientific literature and in documents from governmental institutions. Thus, the implementation of an oil palm farm has been proposed in the Amazon region, specifically in the city of Tailândia, which is the largest oil palm producer in Brazil [20].

2.2.1. Palm Oil Life-Cycle Inventory

The evaluation of a 1-ha FFB production system is described by the flowchart in Figure 1. Sowing occurs in a pre-nursery, and the seedlings develop over three months. The seeds are obtained from a company in Costa Rica (ASD), arrive in the city of Belém by airplane [21] and are transported by truck to Tailândia. Humus from the area surrounding the pre-nursery is used as a substrate for the seedlings. The plastic bags used to hold the seedlings are composed of low-density polyethylene (LDPE) [22]. The fertilizer recommendations for each seedling at this growth stage are 7.5 g of urea, 4.5 g of triple superphosphate (TSP), 3 g of potassium chloride (KCl) and 1.5 g of magnesium sulfate ($MgSO_4$) [23]. The water requirement is approximately 33 L per seedling, and irrigation is performed manually using watering cans [24]. Pest control is conducted manually, from nursery to planting phase, approximately 10% additional seedlings are required due to defective seedlings and pre-germinated seeds that must be eliminated [21]. In one hectare there will be 143 palm trees.

In the nursery, seedlings are transplanted into larger low density polyethylene-LDPE bags filled with local humus. The seedlings remain in the nursery for an additional nine months until they reach the ideal size for planting. The fertilizer recommendations for each seedling at this growth stage are 900 g of urea, 2800 g of TSP, 2050 g of KCl and 900 g of $MgSO_4$ [23]. The water used by the seedlings at this growth stage is approximately 1760 L and is provided by pivots [24]. The pest control at this stage is also manual. At the end of this stage, the seedlings are manually planted in the field.

Figure 1. Flowchart of the production of oil palm fresh fruit bunches.



The rural infrastructure requirements include the opening of roads, the preparation of soil for planting and the cleaning of the area for the implementation of the pre-nursery and nursery. The basic input at this stage is the diesel used by power tractors. The average diesel consumption is approximately 23.56 kg/ha [25]. At the end of the process, 2 kg/ha of *Pueraria phaseoloides*, an N_2-fixing plant, is planted [21].

Maintenance consists of the monitoring of planting throughout the production cycle. After this period, there is basic, manual maintenance consisting of mowing and weeding. Initially, glyphosate is the main product used for chemical treatment around the palm plants, and the basic recommended yearly application rate is 16.5 kg/ha [25]. Maintenance fertilization is also performed in this phase, and based on leaf and soil analysis, it uses 2.5 kg per palm tree of 12:17:10:3 NPK/Mg [22].

Although harvesting is essentially a manual activity, the FFBs are transported to the oil extraction plant by truck. The FFBs must be processed within 72 h after harvest to avoid acidification and the consequent deterioration of the oil [21]. Thus, the crushing plant must be within 50 km of the plantation.

During its whole life-cycle (30 years), palm trees systems fix approximately 130 ton CO_2/ha [26]. The system's emissions are produced by the transport and production of fertilizers, pesticides and plastic bags. The diesel consumed by the fuel trucks, pivot irrigation and electric generators emits 3.14 kg CO_2-eq/kg [27]. Furthermore, the following emissions are associated with fertilizer production: urea = 1.71 kg CO_2-eq/kg (plus 0.02 kg CO_2-eq/kg N in the soil); TSP = 8.63×10^{-1} kg CO_2-eq/kg; KCl = 0.08 kg CO_2-eq/kg; $MgSO_4$ = 3.24×10^{-1} kg CO_2-eq/kg; and pesticides = 4.59 kg CO_2-eq/kg of glyphosate produced. Furthermore, the LDPE production emits 1.78 kg CO_2-eq/kg of plastic produced. Table 1 shows the LCI results of 30 years fresh fruit bunches production in 1 ha in the Amazon region [21–27]. The system was modeled using datasets available in GaBi5 database.

Table 1. LCI of Fresh Fruit Bunches production in 30 years for 1 ha in the Amazon region.

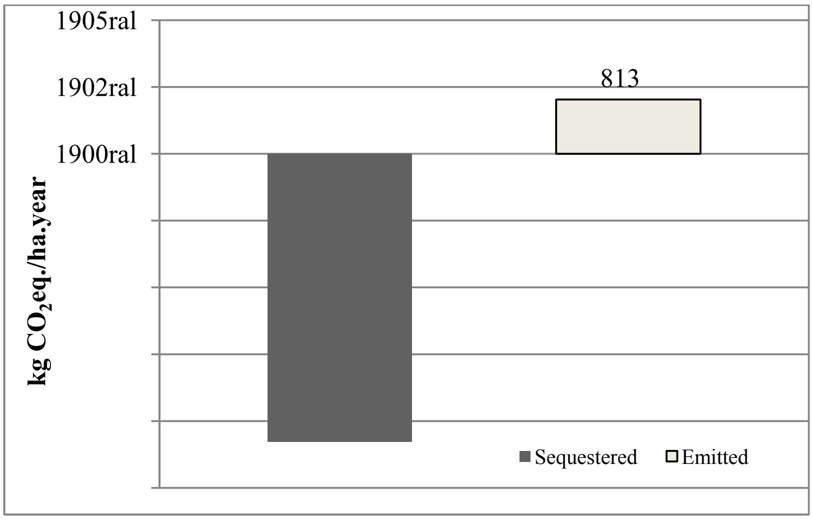
Inputs			**Outputs**		
Material	**Unit**	**Quantity**	**Material**	**Unit**	**Quantity**
Seeds	Unit	160.00	Fresh Fruit Bunches (FFB)	ton	500
CO_2	ton	129.30	Emissions	kg CO_2 eq.	22,380.27
LDPE	kg	2.75	Solid Waste	kg (Plastic bags)	2.75
Water	L	1791			
Urea	kg	1,637.61			
TSP	kg	4,282.86			
KCl	kg	2,240.15			
$MgSO_4$	kg	137.04			
Diesel	kg	3,609.60			
Pesticide	kg	82.5			

2.2.2. Characterization of the Environmental Impacts of Oil Palm

An analysis of the inputs and outputs related to the agricultural phase of 1 ha of oil palm production over the complete crop cycle of 30 years shows that the most important inputs in terms of mass are water and fertilizers, followed by diesel. Despite the culture involving mostly manual operations, there is high diesel consumption by the activities adjacent to the farm, such as the transport of inputs. The most important emissions are related to fertilizers (47.27%) and diesel (51.02%). Plastics (0.02%) and pesticides (1.69%), despite exhibiting high emission factors, show low participation due to scarce use in the system. However, due to a lack of precise information, the emissions associated with the final disposal of these products were not considered.

As a perennial crop whose cultivation involves a low degree of mechanization, oil palm offers great potential as a sink for greenhouse gases. Figure 2 shows that the emitted/sequestered CO_2 ratio is more than 5. This ratio is sensitive to changes such as the use of residues from crushing plants as organic fertilizer or the fluvial transport of inputs. This work involves a comprehensive approach and will stimulate further research to assess the contribution of palm oil for the sustainable development in Amazon.

Figure 2. CO_2 balance in the production of oil palm fresh fruit bunches: agricultural phase.



2.3. The Biodiesel Plant

Biodiesel plants usually operate oil treatment and transesterification units. The operation of these plants is directly related to market demand and maintenance and operation conditions, in addition to crude and refined oil prices. With a current biodiesel yield of approximately 270 m^3/day, the processing units of the plant are essentially units that carry out pre-treatment, transesterification, steam generation and the storage and distribution of products, residues and by-products.

The plants receive a greater amount of refined oil than degummed oil; the latter consists of a mixture of raw materials (vegetable oils, animal fats and residual oils and fats) that are usually derived from soybean, tallow, oil palm, residual fat oil (RFO) and cotton.

2.3.1. Oil Pre-Treatment Unit

The type of pre-treatment stage is determined by the acidity and the amount of phosphorus specific to the oil to be refined. When using cotton and soybean as raw materials, it is necessary to conduct chemical treatment due to their high phosphorus content and high acidity. However, physical treatment is sufficient to decrease the acidity index of tallow and oil palm (20 ppm phosphorus content).

At the end of the refinement, the oil should present a maximum acidity index of 0.1%. Pre-treatments are performed individually for each type of oil; if the oils are mixed, this occurs before transesterification and after the individual treatments.

Soybean oil, in particular, should be treated with phosphoric acid and caustic soda to remove phosphatides and free fatty acids. After the reaction is complete, the fluid passes through a centrifugation step to remove soaps and other residual products. During the pre-treatment step, co-products such as fatty acid and gum are produced. All of these co-products are marketed or used for specific applications.

2.3.2. Transesterification Unit

Transesterification is a chemical process involving a catalyst-assisted reaction between methanol and oil for the purpose of obtaining biodiesel. In the plant, the mixture of the methanol, catalyst and oil is performed in the production line.

Transesterification generally involves more than one step, and each step has a residence time of 20 min. The resulting product is overflowed to a separation tank, where glycerin (30%) diluted in methanol (30%), water and salt are separated from the biodiesel.

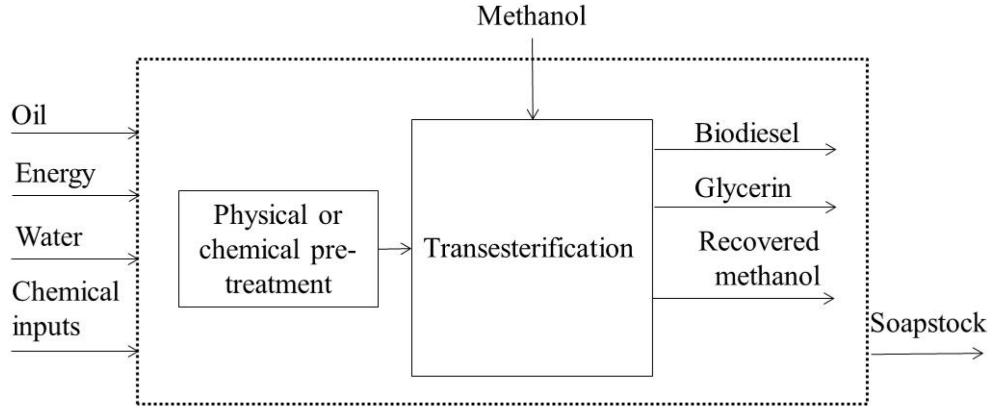
The biodiesel is neutralized with HCl to achieve a pH in the range of 5 to 7 to deactivate the catalyst (which was not separated in the previous step). The biodiesel is then washed to remove excess nonpolar compounds (methanol and NaCl). This process continues for 20 min, and the biodiesel attains a pH between 5.5 and 6. The same washing process is performed for the glycerin.

The excess methanol added to the process is recovered and reused, as is the biodiesel wash-water. Glycerin containing 10% water and 0.1% methanol is recovered after transesterification and also marketed.

2.4. Environmental Impact Assessment of Biodiesel Production

Figure 3 shows the system boundaries for the industrial stage of biodiesel production. It is clear that in a complete assessment of the life-cycle, it is also necessary to evaluate the agricultural phase of oil production.

Figure 3. Major steps involved in the industrial phase of biodiesel production.



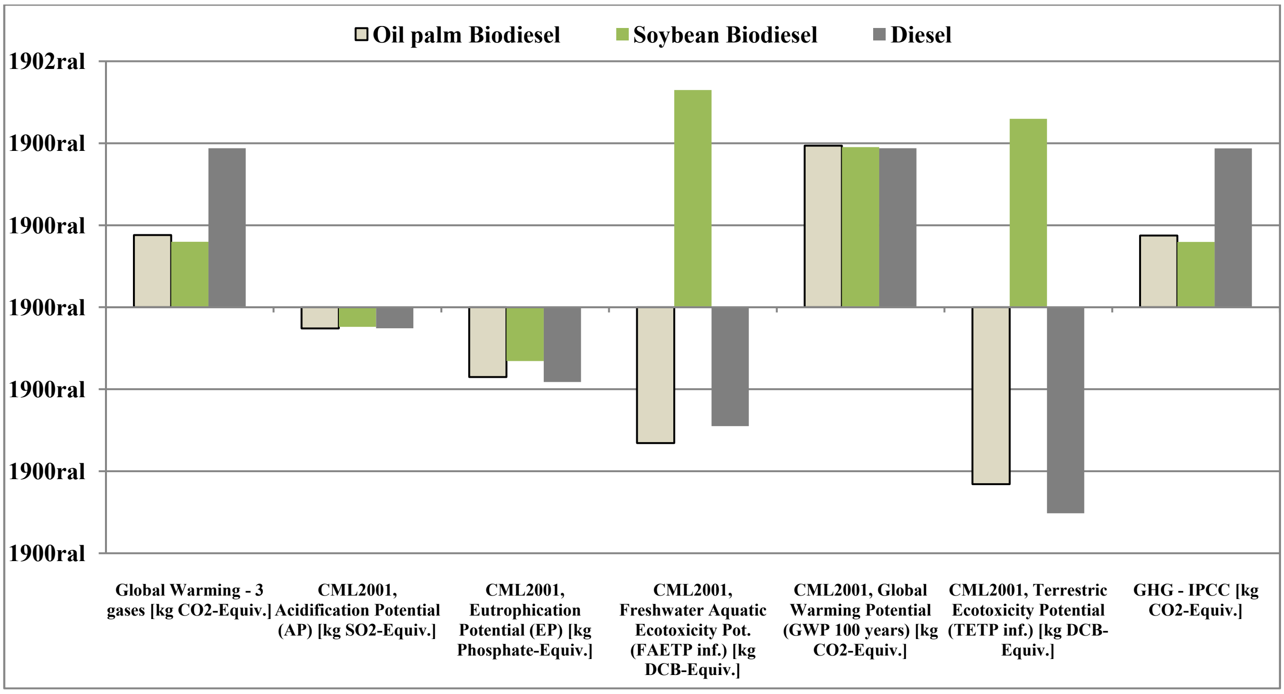
Therefore, the agricultural production stages associated with palm and soy oil were incorporated into the analysis. The implementation of this system is based on developmental analyses of the diesel and biodiesel life-cycle inventories for oil palm and soybean, with the agricultural phase developed from the secondary data.

The environmental impact protocols used for fuel assessment, the methods of the CML2001 and Greenhouse Gases—Intergovernmental Panel on Climate Change (GHG-IPCC), are compatible with the production systems and are accepted internationally for this type of comparison. The three protocols used to characterize environmental impacts are:

(i) Global Warming—3 gases (kg CO_2-eq);
(ii) GHG-IPCC (kg CO_2-eq); and
(iii) CML2001:
   a. CML2001, Acidification Potential (AP) (kg SO_2-eq);
   b. CML2001, Eutrophication Potential (EP) (kg phosphate-eq);
   c. CML2001, Aquatic Ecotoxicity Potential (FAETP) (kg DCB-eq);
   d. CML2001, Global Warming Potential (GWP 100 years) (kg CO_2-eq); and
   e. CML2001, Terrestrial Ecotoxicity Potential (TETP) (kg DCB-eq).

A more detailed analysis of the environmental impacts of the life-cycle of each fuel is presented in Figure 4, compared to diesel fuel from a Brazilian Company.

Figure 4. Environmental impact characterization. Comparative analyzes of biodiesels from oil palm and soybean, as well as diesel.



The data used for LCA construction was based on secondary and primary information (soybean oil, soybean biodiesel, palm oil and palm biodiesel and diesel). The bar graph indicates the differences between the categories Global Warming and GHG-IPCC compared with CML2001, GWP that were caused by not accounting for the biotic CO_2 emissions. Furthermore, Figure 4 indicates the lower environmental impacts of biofuels with respect to CO_2 emissions, when compared with diesel.

For biofuel-based systems, the impacts associated with fuel consumption for agricultural transport and practices, as well as those related to fertilizer and pesticide production, in the categories of acidification, eutrophication and aquatic and terrestrial ecotoxicity were assessed.

Biofuel production has a greater impact on some categories of environmental impacts associated with agricultural stages and fuel consumption in the industrial phase. In this context, the life-cycle of soybean biodiesel is associated with higher values compared with oil palm biodiesel in all of these categories. The greatest impact is associated to agricultural implements as fertilizer, pesticide and transportation.

3. Bioethanols

3.1. First-Generation Ethanol

Following the guidelines of Life Cycle Assessment (LCA) and Life Cycle Costing (LCC), this chapter aimed at quantifying the costs of processes and flows included in the production of anhydrous ethanol, such as use of machinery, fuel consumption, transportation, labor and industrial and agricultural operations. Notably, ethanol LCC cannot be dissociated from LCA, which aims at analyzing the general environmental issues to establish parameters that delimit the inputs and outputs of the system limits included in an overall system.

LCC's methodology is an important tool for analyzing the economic viability of ethanol as an alternative fuel source. This tool addresses the elements that generate costs over the life-cycle of a product or service [28]. The development of improved measures related to cost reduction during both sugarcane cultivation and ethanol production is a strategic action to enhance the potential of ethanol compared with fossil fuels [29]. Moreover, this renewable energy source can promote a market favorable to ethanol producers and investors, thus contributing to the implementation of economic and social policies associated with the use of ethanol in Brazil.

In the present study, the primary stages of the life-cycle of ethanol are the agricultural and industrial stages, extra processes, disposal operations and the reuse of by-products. Within these four main processes, there are sub-processes that are interconnected by mass and energy flows, along with their respective costs, which will provide the necessary information to conduct impact analysis based on mass and energy balances, emissions and costs.

3.1.1. Goal Setting

The total of all the costs associated with the operations and the inputs applied to the processes that constitute the ethanol supply chain were determined. For this purpose, secondary data was collected to characterize the technological model mapped from the tillage of soil for sugarcane cultivation to product distribution (cradle-to-gate).

Following the guidelines of the LCA and LCCA methods, the costs of the processes and flows included in the production of anhydrous ethanol, such as machinery use, fuel consumption, transportation, labor and industrial and agricultural operations, were quantified.

3.1.2. Scope Definition

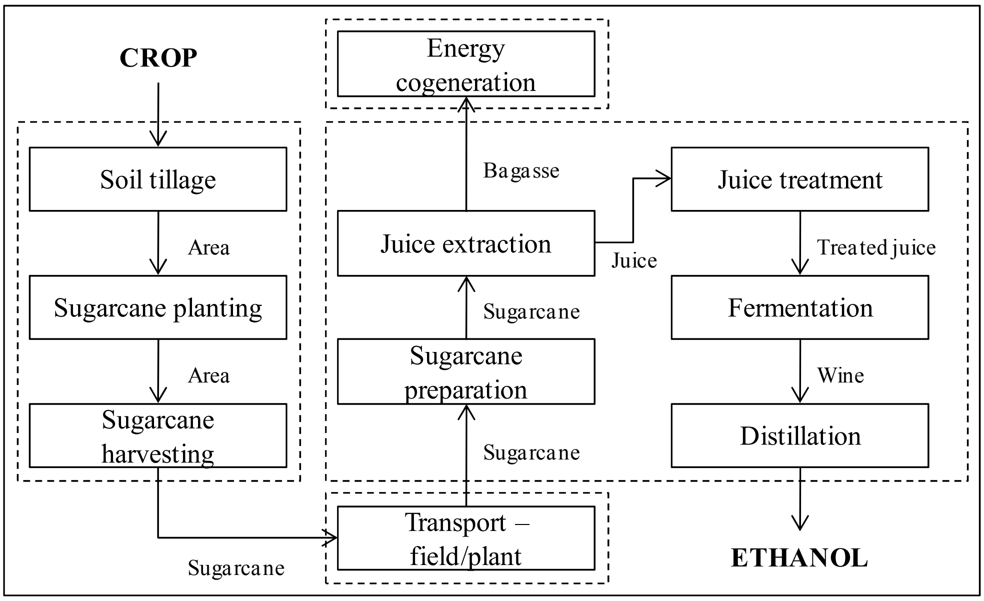
In this study, the goal of the system, as defined by ISO14040 [30], was the commercialization of anhydrous ethanol for use as a vehicle fuel. To meet this goal, the functional unit was defined as the costs and environmental impacts of the use of 1 kg of anhydrous ethanol mixed with gasoline (25% v/v in gasoline) and used in medium-size passenger vehicles.

Based on the definition of the functional unit, the reference flux was delimited so that all of the secondary data collected would relate to this measurement of the components and operations required to fulfill the goal of the system. Thus, the reference flow was expressed per 1 kg of anhydrous ethanol with 0.3% water and a density of 0.789 g/cm^3.

The system's boundary was defined so that the main production units would be analyzed separately and joined to form a boundary, which can be considered a major process, with its respective inputs and outputs as well as auxiliary processes that constitute the delimited boundary. In this case, the system boundary consists of internal limits that are essentially defined by the agricultural and industrial stages of ethanol production. The cogeneration of energy and transportation from the field to the industrial phase are extra limits that contain processes auxiliary to the system's boundary.

The agricultural and industrial stages were fragmented to detail the flows included in many existing processes, resulting in the following divisions: (1) the agricultural phase—soil cultivation and the planting and harvesting of sugarcane; and (2) the industrial phase—sugarcane preparation, sugarcane juice extraction and juice treatment, fermentation and distillation. Figure 5 shows the system boundaries. Each process is a compilation of the ethanol-producing steps, which connect through the flow of outputs interconnected with the subsequent input of the process along the chain.

Figure 5. System boundaries for anhydrous ethanol production.



3.1.3. Characterization of the Sugarcane Cultivation Phase

This life-cycle phase was based on sugarcane cultivation using the ratoon cropping system, which consists of consecutive annual cuttings following the initial cutting [31]. Prior to the first year of planting, the soil is prepared via the intensive application of a fertilizer with a high percentage of phosphorus. Next, the seeds are distributed, the furrows are covered, and there is an additional application of fertilizers and herbicides. The sugarcane is finally ready for the first cutting after 15 months [32].

The collected secondary data refer to the 2009/2010 Brazilian crop [33,34]. The costs, values and other flows correspond to an area of 1 ha of cultivated sugarcane harvested mechanically. Moreover, during the five years in which agricultural production was considered, 450 ton/ha (approximately 90 ton/ha/year) of sugarcane [33], 108 ton/ha of bagasse and 26.56 ton/ha of straw were produced [35]. To adjust to the reference flow (associated with 1 kg of anhydrous ethanol), the data were converted to a scale factor related to the adopted functional unit.

3.1.4. Characterization of the Industrial Phase of Ethanol Production

The industrial phase contributes significantly to ethanol production in terms of the costs of the operations that form the supply chain. Therefore, the LCCA should be performed carefully due to the great importance of this step for the impact analysis. The most representative consumption and cost data, considering the mass and energy flows within these processes, were obtained by Xavier [34].

The assessment of the industrial phase considered a plant that receives sugarcane harvested without burning, which is then washed and chopped to undergo juice extraction in mills. After milling, the bagasse is separated from the juice. The bagasse and the straw are sent to the cogeneration system, and the extracted juice is chemically treated to form the must, which is mixed with yeast. The must/yeast mixture is then fermented, and the sugars are converted to ethanol and CO_2. After fermentation, the resulting wine is centrifuged to separate the yeast, gases, minerals and unfermentable sugars. After this stage, the centrifuged wine undergoes distillation to obtain hydrous ethanol at a concentration of approximately 96% °GL and undergoes dehydration to obtain anhydrous ethanol at a concentration of 99.7% °GL [35].

3.1.5. Assessment of Cost and Environmental Impacts

A determination of the cost balance over the ethanol life-cycle that considered the data related to the inputs and outputs, machinery and labor was performed using Gabi Academic 5.0 software. The costs associated with 1 ton of sugarcane present in the outflows were quantified, as were the costs per ha of the agricultural machinery and field labor. Because the economic data were simultaneously included in the mass and energy flows of the processes, the LCA and LCCA were conducted simultaneously to obtain information about the economic and environmental impacts of the life-cycle of anhydrous ethanol.

To match the reference flow, the outflows were converted to the scale required by the industry to produce 1 kg of anhydrous ethanol. Figure 6 shows the total relative costs per production stage. The results suggest that the steps of sugarcane harvesting (the agricultural phase), juice treatment and fermentation (the industrial phase) are associated with the highest costs in the supply chain. The inputs are responsible for the greatest proportion of the costs of these three steps, although the hours/machine costs are significant for the soil tillage step. The total cost was found to be R$ 13.62/kg ethanol; 24.05% of this amount was derived from the agricultural phase and 75.95% from the industrial phase.

Similarly, based on the CML2001 method with the indices updated in November 2009, the environmental balance was quantified for each production stage (Figure 7) considering the GWP (100 years) and AP impact categories.

Figure 6. Relative costs per stage of anhydrous ethanol production.

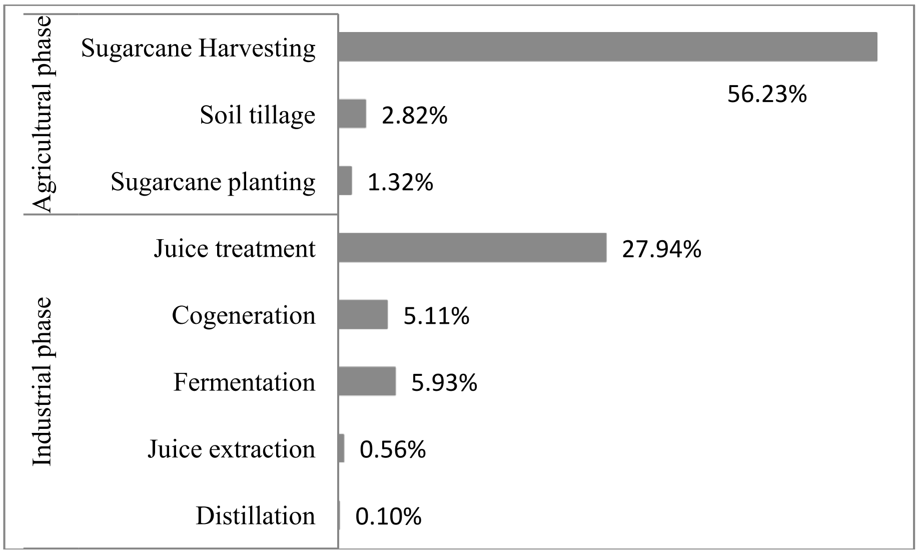
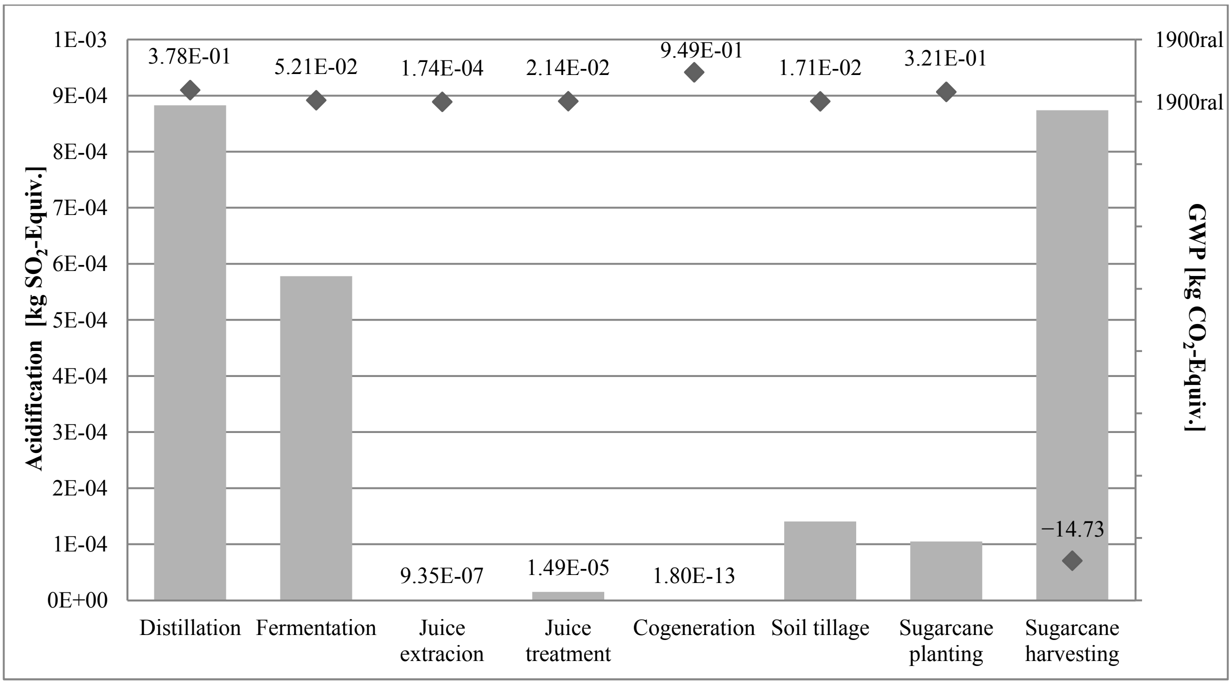


Figure 7. Environmental balance of the anhydrous ethanol production process by impact category.



It was noted that the cogeneration of energy was responsible for the major impact of the GWP balance (0.94 kg CO_2-eq/kg ethanol). This result was directly related to the emission of pollutant gases by the boiler, with the highest indices being related to the CO_2 and soot released from burning bagasse and straw. During the mechanized harvest stage, a high level of avoided emissions was achieved, which was primarily related to the balance between the CO_2 uptake and the emissions derived from harvesting without burning, which corresponded to 14.84 and 0.1 kg CO_2-eq/kg ethanol, respectively.

Other gases were emitted in small amounts, such as CH_4, N_2O, sulfur hexafluoride, dichloromethane and tetrafluoromethane. Therefore, the balance was negative for mechanized harvesting, with −14.73 kg CO_2-eq/kg anhydrous ethanol produced.

The distillation process was associated with the highest indices of acidification potential compared with the other steps of the industrial stage. Of the 8.83×10^{-4} kg SO_2-eq/kg ethanol, 70.5% was SO_2, 26.6% was NO_x, and 1.3% was ammonia; *i.e.*, these three chemical compounds constituted the majority of the emissions. In the agricultural phase, the mechanized sugarcane harvesting step showed the highest acidification potential, 8.74×10^{-4} kg SO_2-eq/kg ethanol, with the following proportions: 22.61% SO_2, 77.22% NO_x and 0.12% NH_3. These compounds are acidifying components that affect the soil, water and ecosystems when released into the environment. The high concentration of N_2O in the ethanol supply chain is the main indicator of the magnitude of the acidification potential.

An analysis of the economic and environmental impacts of the ethanol life-cycle was performed using a static technological model based on a hypothetical production scenario. Therefore, the adopted methodology did not encompass productive or market dynamics. The major contribution of the study lies in the mapping of the economic-environmental outlook for the identification of links in the chain that are amenable to optimization, which is a support tool for strategic decision-making processes in the alcohol sector based on cost and sustainability diagnostics.

3.2. Second-Generation Ethanol

Currently, the production of first-generation ethanol results in the exploitation of only one-third of the energy contained in sugarcane. The production of ethanol from hemicellulose and cellulose has been considered feasible, provided that there is a thorough analysis of the pre-treatment, hydrolysis and fermentation processes. Lignocellulosic material is a natural product that is mainly composed of cellulose, hemicellulose and lignin. Different pre-treatment combinations involving mechanical and chemical processes can be applied. In the current race toward sustainable development, the increased use of biomass is associated with significant environmental gains [36].

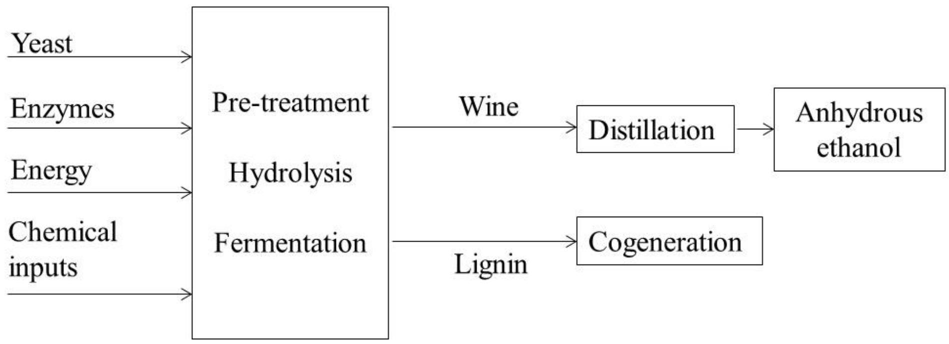
A future goal is the simultaneous occurrence of these transformations in fewer reactors, which requires the use of microorganisms that are capable of fermenting both hemicellulose and cellulose with high yields. Although there has been some success in achieving this goal, the fermentation of mixed-biomass sugars has not yet reached a commercially viable plateau [17]. It remains necessary to consider the harmful fermentation inhibitors present in the hydrolysate (e.g., acids, furans and phenolic compounds), which must be removed if present at high concentrations.

Sugarcane is widely cultivated in Brazil, Cuba, Australia, South Africa, Peru, Mexico and India. There is high sugarcane production in Brazil, corresponding to approximately 425 million tons per year, and Brazilian ethanol production has been increasing rapidly, reaching 18 billion gallons in 2007 [36]. The transformation of sugarcane into ethanol results in two major by-products, thermal energy and bagasse [37].

Sugarcane bagasse can be considered either as a waste product that affects the environment or as a resource, when the appropriate recovery technologies are implemented. In the latter case, sugarcane bagasse offers the possibility of full valorization when it is processed into commodities with domestic and international market potential [38]. Gonçalves *et al.* [39] performed an analysis of an integrated process for the conversion of sugarcane bagasse and straw. That study concluded that it is possible to obtain various derivatives of these lignocellulosic materials from chemical processes using the direct, catalytic or aggressive conversion of cellulose, hemicellulose and lignin [39].

Currently, ethanol production is performed using solely first-generation technologies, in which the glucose present in sugarcane is fermented and converted into ethanol [17]. Figure 8 shows a simplified diagram of the process of ethanol production from sugarcane bagasse.

Figure 8. Flowchart of the pre-treatment, hydrolysis and fermentation stages of the production of second-generation ethanol.



The difference between the first- and second-generation technologies occurs at the beginning of the process, where biomass is subjected to hydrolysis (saccharification). This process (hydrolysis) involves the incorporation of water into cellulose and hemicellulose, which converts them into sugars [40]. Following the saccharification step, a fermentation step is performed, which converts sugars into alcohol, followed by the distillation step, which separates the ethanol from the remaining components of the must (primarily water) [17]. Lignin cannot be used for ethanol production; however, it may be used in a cogeneration process [40].

When considering the application of the technological model of second-generation ethanol production, the aim is to aggregate a group of distinct and specific operation units, including pre-treatment, hydrolysis and fermentation, within a first-generation ethanol production industrial complex.

A comparison of the introduction of bagasse cellulose pre-treatment and lignin burning with the original ethanol production process is presented in Figure 9. LCA modeling was made with primary data from an important Brazilian company, and is subjected to confidentiality agreement. The results indicate that the effect of the higher efficiency of sugarcane carbon use for ethanol production is reflected in the smaller amount of sugarcane required to produce the same amount of ethanol and, thus, the smaller amount of CO_2 sequestered in the agricultural phase. This industrial phase of cellulosic ethanol production also emits less CO_2 because only lignin from bagasse is burned to produce steam and electricity.

In addition, Figure 9 illustrates the redistribution of the CO_2 emitted during the industrial phase. A smaller amount of CO_2 is emitted via cogeneration due to the smaller amount of lignin being burned, the lower CO_2 emissions during first-generation fermentation and the increase in the second-generation cellulose hydrolysis and fermentation phases.

Figure 10 presents a sensitivity analysis of first- and second-generation ethanol production with varied amounts of bagasse used for the production of second-generation ethanol. The results show that even when 100% of the bagasse is used to produce second-generation ethanol, some sequestration of CO_2 remains in the total balance of the production process, and this value is only 83% of the maximum possible value.

Figure 9. Comparison of the industrial, agricultural and other phases of first- and second-generation ethanol production.

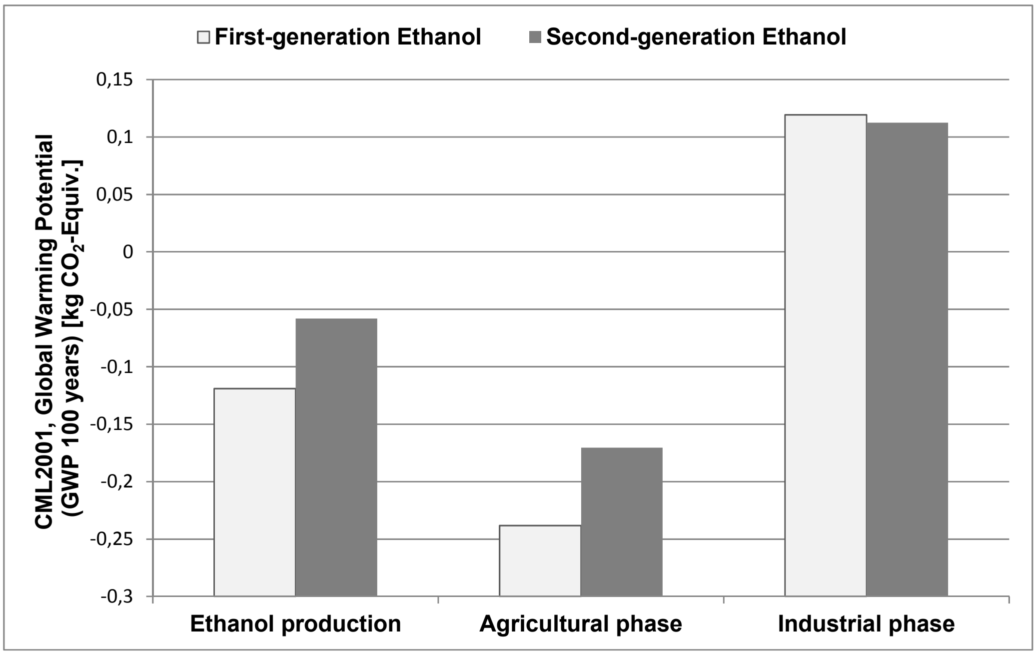
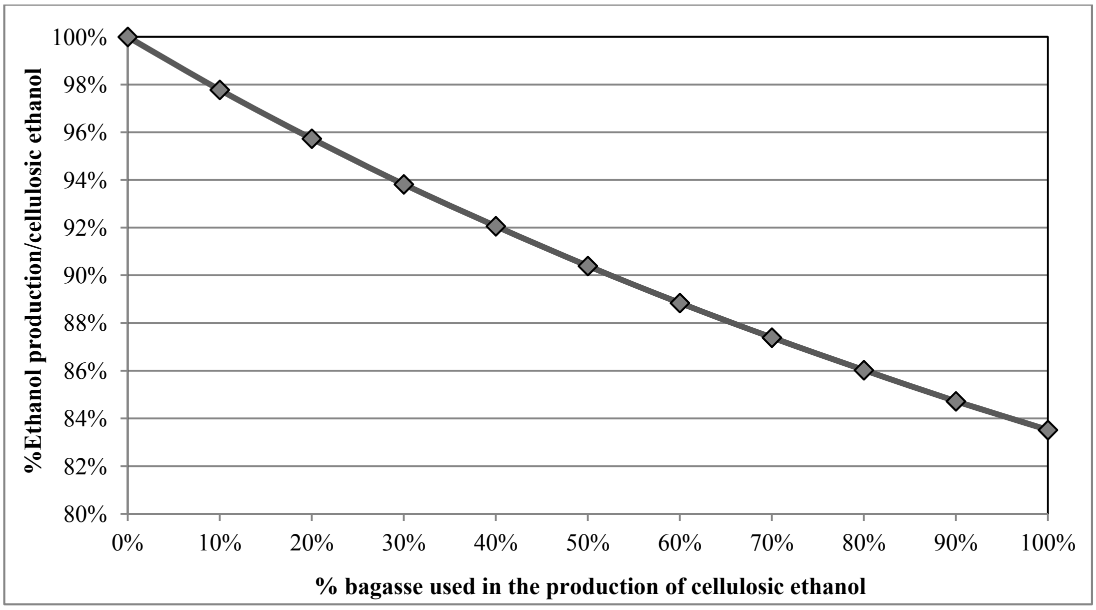


Figure 10. Plot of the results of the sensitivity analysis of the amount of bagasse used for the production of second-generation ethanol in terms of the CO_2-eq balance.



4. Economic Impacts of Ethanol Production Examined via the Structural Path Analysis Method

The growth in the global demand for biofuels is mainly reflected in the goals of the transport and energy policies adopted by major energy markets, such as the European Union and the United States.

United States has adopted a Renewable Fuel Standard (RFS2) that mandates an increase in the use of renewable biofuels, an significant portion of which must be derived from lignocellulosic biofuels by 2022 [41]. In 2009, The European Union adopted the Renewable Energy Directive (RED), which promote the use of renewable energy sources and established a requirement that 10% of transport energy be based on renewable energy sources. Considering specific sustainability criteria, RED has been projected for achieving a cumulative growth rate in the use of renewable energy of 112% from 2010 to 2020 [41]. As several authors have maintained [41–44], these policies aim at increasing the production and use of energy derived from renewable natural resources and note some criteria to achieve sustainability in the biofuel sector.

One method that can be used to examine the environmental and economic performance of the different economic activities of a country or region is the Structural Path Analysis [44–47]. This methodology uses as database the input-output tables, which are published by the Brazilian Statistical Institute, to obtain the core of this analysis, the technical coefficient matrix **A**. Some of the advantages of a SPA are: (a) the analysis has a complete perspective of the economy; (b) this approach avoids truncation problems usually found in LCA; and (c) it uses a database representing completely the technology used in the country or region considered. On the other hand, the main disadvantage is the high aggregation level of the database, and in many cases, the age of the data used. More description about SPA is found in the literature [44–47]. SPA computes the economic and/or environmental performance of a given economic sector by detailing the complete supply chains, known in the SPA literature as input paths, using a cradle-to-gate perspective. This methodology identifies, quantifies and ranks the input paths that more contribute to the economic and environmental performance of a given sector.

This section of the article presents the results regarding the identification of the input paths that make the largest contribution to the economic and environmental performance of Brazilian ethanol sector. In this context, we analyzed two economic factors, the Gross Domestic Product (GDP—R$ million) and the number of jobs created (1000); and two environmental factors, CO_2 emissions (millions of kg of CO_2 equivalents) and fuel consumption (TJ). In addition, this analysis enables the identification of the contributions of SPA to the analysis of the environmental and social life-cycles. It is important to highlight that this is the first time that a SPA is applied to assess the environmental and economic performance of the Brazilian ethanol.

The conventional input-output model analyzes the intersectorial relationships within an economy. In 1970 [48] presented a extension of the conventional input-output model in which an analysis of “undesirable outputs”, *i.e.*, by-products or pollution flows, from the production processes of various industries was incorporated into the input-output model. Since that time, the input-output approach has been employed in both economic and environmental applications. The starting point of the input-output model is the matrix of technical coefficients A, where each column represents the input technology of each sector, and it is obtained by the relation between the intersectorial transactions matrix and the total output vector.

This mathematical model enables the description of economic factors, such as GDP and employment, and/or environmental factors, such as CO_2 emissions and energy consumption. This approach mathematically identifies the effects of producing a particular product, linking it with the intensity of economic and/or environmental factors and providing the global effects of the analyzed factors by sector.

However, these global effects by sector can be disaggregated into input paths through an SPA [49]. An SPA computes the economic and/or environmental performance of a given production sector via detailing the complete supply chain using a cradle-to-gate perspective, including the identification, quantification and rank of the input paths that make the greatest contribution to the performance of a given sector [45,50,51].

SPA is based on the process of unraveling Leontief's inverse matrix L using the various sectorial interactions represented by the technical coefficient matrix [52–55] and on the incorporation of the path multiplier concept [49]. The original form of the structural path approach proposed by [38] consists of three measures of the influence of the origin sector, *i*: on the destination sector, *j*: the direct influence, total influence and global influence of each input path [46,49,51,56].

SPA Results

SPA was employed to examine nearly 800 input paths for each factor being studied, and the final demand of the ethanol sector, known in LCA approach as functional unit, for 2010 is R$ 5,202,102. The three-top input paths identified in this SPA represent more than 73% of the total contribution of each factor, and they are shown in Table 2.

Table 2. Top input paths identified in the SPA for each factor.

Rank	Input Paths	Values	Units	Order	Total impact %
1	Fge←Sc	951.3	10×10^6 kg CO_2	1	39.2
2	Fge	873.4	10×10^6 kg CO_2	0	36.0
3	Fge←Tra	80.4	10×10^6 kg CO_2	1	3.3
1	Fge←Sc	10,000.1	TJ	1	64.4
2	Fge←Tra	1,415.0	TJ	1	9.1
3	Fge	909.8	TJ	0	5.9
1	Fge←Sc	89.8	10×10^3 jobs	1	38.7
2	Fge←Alf	50.0	10×10^3 jobs	1	21.5
3	Fge	30.8	10×10^3 jobs	0	13.2
1	Fge	2,293.9	10×10^6 R$	0	47.6
2	Fge←Sc	1,019.1	10×10^6 R$	1	21.1
3	Fge←Alf	264.6	10×10^6 R$	1	5.5

Abbreviations: Fge: sugarcane derived ethanol; Sc: sugarcane; Tra: transport; Alf: agriculture, livestock and silviculture; TJ: Terajaule.

Therefore, the total CO_2 emissions from the ethanol industry due to fuel combustion and the electricity consumption of the external network were 2427.7 million kg CO_2-eq in 2010. This cradle-to-gate assessment of CO_2 emissions identified two main input paths that influence the industry's environmental performance: the sugarcane sector (ethanol←sugarcane), and the direct contribution of the industry. The total energy consumption of the ethanol industry was 15,535.67 TJ in 2010, with the sugarcane industry being responsible for 64.37% of this total.

According to 2002–2007 data from the Brazilian Statistical Institute and the Brazilian Sugarcane Industry Association (UNICA) [41], 70% of the direct jobs in the sugar-alcohol industry occur in the agricultural phase and 30% in the industrial phase. Here was identified that the sugarcane that feed the ethanol sector represents 38.68% of total employment generation. The jobs created by the sugarcane industry require minimal education; however, this is changing because of the introduction of mechanized harvesting, which is increasing the skill level necessary in the industry and, consequently, the income level of workers [42,57]. The ethanol industry has a direct influence of 13.25% on the total job creation; on average, this industry requires mid-level skill jobs. The commerce and service industries also have an important influence on employment generation, which is related to the intensive maintenance and installation services involved in the ethanol industry.

Finally, the ethanol sector has a direct influence of approximately 48% on generation of GDP, and the sugarcane sector (ethanol←sugarcane) contributes 21%. Together, these sectors contribute 69% of the GDP of the industry.

5. Conclusions

On the basis of the results presented in this study, it can be concluded that the use of biofuels in transportation can lead to the mitigation of some environmental impacts, such as greenhouse gas emissions. However, there must be a greater effort to improve agricultural management practices to decrease the consumption of fuel, fertilizers and herbicides.

With respect to ethanol production, it is concluded that there must be a greater consideration of aspects of the ethanol life-cycle. The use of mechanical harvesting, for example, reduces emissions from sugarcane burning; however, it also increases the cost of machinery and the environmental impacts of soil compaction and the increased use of diesel.

The use of straw in cogeneration should also be considered because it generates more electricity but also larger amounts of polluting gases from the boiler. Additionally, this straw can no longer to be used as an organic fertilizer, which may increase the costs associated with fertilizer use. Finally, the allocation of bagasse for cogeneration, in contrast with its use in the production of second-generation ethanol, is another factor that must be thoroughly analyzed because this decision involves a balance between environmental and economic costs.

References and Notes

1. Gielen, D.J.; Fujino, J.; Hashimoto, S.; Moriguchi, Y. Biomass strategies for climate policies? *Clim. Policy* **2002**, *2*, 319–333.
2. Quaglio, S. *Yearbook of Brazilian Energy Analysis* [in Portuguese]; Análise Editorial: São Paulo, Brazil, 2011.
3. Narayanaswamy, V.; Altham, J.; Berkel, R.V.; McGregor, M. *Methodological Framework for Application of Environmental Life Cycle Assessment (LCA) to Australian Grains*; Curtin University of Technology: Perth, Australia, 2003.

4. Pegoraro, L.A. *Desenvolvimento de Fatores de Caracterização para Toxicidade Humana em Avaliação do Impacto do Ciclo de Vida No Brasil [Development of Characterization Factors for Human Toxicity in the Assessment of Life Cycle Impact in Brazil]*; Mestrado em Engenharia, Programa de Pós-graduação em Engenharia Mecânica e de Materiais, Universidade Tecnológica Federal do Paraná: Curitiba, Brazil, 2008.
5. Singh, A. Olsen, S.I. A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels. *Appl. Energy* **2011**, *88*, 3548–3555.
6. Nigama, P.S. Singh, A. Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* **2011**, *37*, 52–68.
7. Singh, A.; Pant, D.; Olsen, S.I.; Nigam, P.S. Key issues to consider in microalgae based biodiesel production. *Energy Edu. Sci. Technol. Part A Energy Sci. Res.* **2012**, *29*, 687–700.
8. Luo, L.; van der Voet, E.; Huppes; G. Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil. *Renew. Sustain. Energy Rev.* **2009**, *13*, 1613–1619.
9. IndexMundi. World Biodiesel Production by Year. Available online: http://www.indexmundi.com/energy.aspx?region=xx&product=biodiesel&graph=production (accessed on 6 January 2012).
10. Yadava, D.K.; Vasudev, S.; Singh, N.; Mohapatra, Y.; Prabhu, K.V. Breeding Major Oil Crops: Present Status and Future Research Needs. In *Technological Innovations in Major World Oil Crops*; Springer: New York, NY, USA, 2012.
11. FAOSTAT. Faostat Database Query: Soybean Production. Available online: http://faostat.fao.org/site/339/default.aspx (accessed on 12 June 2006).
12. Dalgaard, R.; Schmidt, J.; Halberg, N.; Christensen, P.; Thrane, M.; Pengue, W.A. LCA of Soybean Meal. *Int. J. Life Cycle Assess.* **2008**, *13*, 240–254.
13. CONAB-Companhia Nacional de Abastecimento [Brazilian Food Supply Company]. *Acompanhamento da Safra Brasileira: Grãos, oitavo levantamento, Maio 2012 [Monitoring of Brazilian Harvest: Grains, Eighth Survey, May 2012]*; CONAB: Brasília, Brazil, 2012; 631.165(05), C743b.
14. IEA-International Energy Agency. *CO_2 Emissions from Fuel Combustion: Highlights*; IEA: Paris, France, 2012. Available on line: http://www.iea.org/publications/freepublications/publication/CO2emissionfromfuelcombustionHIGHLIGHTS.pdf (accessed on 6 January 2013).
15. Ministério da Agricultura, Pecuária e Abastecimento—MAPA. *Agronegócio Brasileiro em Números [Brazilian Agribusiness in Numbers]*; Available online: http://www.agricultura.gov.br/comunicacao/publicacoes (accessed on 6 January 2013).
16. Banco Nacional de Desenvolvimento Economico e Social-BNDES. *Bioetanol de Cana-de-Açúcar: Energia Para o Desenvolvimento Sustentável [Bioethanol from Sugarcane: Energy for Sustainable Development]*; BNDES: Rio de Janeiro, Brazil, 2008.
17. Xavier, J.H. Análise de Ciclo de Vida (ACV) da Produção Agrícola Familiar em Unaí-MG: Resultados Econômicos e Impactos Ambientais [Life Cycle Analysis (LCA) of Family Agricultural Production in Unai, Minas Gerais: Economic Results and Environmental Impacts]; Master’s Thesis, Centro de Desenvolvimento Sustentável, Universidade de Brasília,. Brasília, Brazil, 2003.

18. ANP—Agência Nacional de Petróleo. National Agency of Petroleum] Boletim Mensal de Biodiesel. Available online: http://www.anp.gov.br/?pg=60127&m=&t1=&t2=&t3=&t4=&ar=&ps=&cachebust=1336745196714 (accessed on 6 January 2012).
19. NAE—Núcleo de Assuntos Estratégicos da Presidência da República [Strategic Issues Office from the Presidency of the Republic]. *Cadernos NAE 2—Biocombustíveis [Biofuels]*; NAE: Brasília, Brazil, 2005.
20. EMBRAPA. *Tecnologias de Produção de Soja: Região Central do Brasil 2011 [Soy Production Technologies: Central Region of Brazil 2011]*; Embrapa Soja: London, UK, 2010.
21. EMBRAPA. *Complexo Agroindustrial de Biodiesel no Brasil: Competitividade das Cadeias Produtivas de Matérias-Primas [Agro Industrial Complex of Biodiesel in Brazil: Competitively of Raw Materials Chain]*; Embrapa Agroenergia: Brasília, Brazil, 2010.
22. Viégas, I.J.; Müller, A.A. *A Cultura do Dendezeiro na Amazônia Brasileira [Oil Palm Cultivation in the Brazilian Amazon]*; Embrapa Amazônia Oriental, Manaus, Embrapa Amazônia Ocidental: Belém, Brazil, 2000.
23. SEAGRI—Secretaria de Agricultura, Irrigação e Reforma Agrária [Secretariat of Agriculture, Irrigation and Agrarian Reform], BA. Cultura Dendê [Oil palm culture]. Available online: http://www.seagri.ba.gov.br/Dende.htm (accessed on 6 January 2012).
24. EPE—Empresa de Pesquisa Energética [Energy Research Office]. Potencial de Redução de Emissões de CO_2 em Projetos de Produção e Uso de Biocombustíveis [Potential for Reducing CO_2 Emissions in Production Projects and the Use of Biofuels]. Available online: http://www.epe.gov.br/Petroleo/Documents/Estudos_29/EPE%20-%202%C2%BA%20Biocombust%C3%ADveis%20x%20MDL.pdf (accessed on 6 January 2012).
25. Furlan, J.; Kaltner, F.J.; Azevedo, G.F.; Campos, I.A. *Biodiesel: Porque tem que ser Dendê [Biodiesel: Why It Has to Be Oil Palm]*, 1st ed.; Embrapa Amazônia Oriental, PALMASA: Belém, Brazil, 2006.
26. CETESB—Companhia Ambiental do Estado de São Paulo [Environmental Company of São Paulo]. Metodologia Simplificada de Cálculo das Emissões de Gases do Efeito Estufa de Frotas de Veículos no Brasil [Simplified Methodology for Calculating Emissions of Greenhouse Gases from Vehicle Fleets in Brazil]. Available online: http://www.sinaldetransito.com.br/artigos/gases_efeito_estufa.pdf (accessed on 6 January 2012).
27. Germer J.; Sauerborn J. Estimation of the impact of oil palm plantation establishment on greenhouse gas balance. *Environ. Dev. Sustain.* **2008**, *10*, 697–716.
28. Finnveden, G.; Moberg, A. Environmental systems analysis tools—An overview. *J. Clean. Prod.* **2008**, *13*, 1165–1173.
29. Nguyen, T.L.; Gheewala, S.H. Life cycle cost analysis of fuel ethanol produced from cassava in Thailand. *Int. J. Life Cycle Assess.* **2008**, *13*, 564–573.
30. International Organization for Standardization (ISO). *14040. Environmental Management—Life Cycle Assessment—Principles and Framework*; ISO: Geneva, Switzerland, 2006.
31. Leal, M.R. *Technological Evolution Processing of Sugar Cane for Ethanol and Electricity* [*Bioethanol from Sugar Cane: R & D for Productivity and Sustainability*]; Blucher: São Paulo, Brazil, 2010.

32. Suiran, Y.; Jing, T. Economic, energy and environmental evaluation of biomass-based fuel ethanol projects based on life cycle assessment and simulations. *Appl. Energy* **2009**, *86*, S178–S188.
33. AGRIANUAL—Anuário da Agricultura Brasileira. *Yearbook of Brazilian Agriculture*; Informa Economics: São Paulo, Brazil, 2009.
34. Xavier, C.E.; Zilio, L.B.; Sonoda, D.Y.; Marques, P.V. *Custos de Produção de Cana, Açúcar e Etanol no Brasil: Safra 2008/2009 [Production Costs for Sugarcane, Sugar and Ethanol in Brazil: 2008/2009 Crop]*; Report for the National Confederation of Agriculture: Piracicaba, Brazil, 2009.
35. Ripoli, T.C.; Ripoli, M.L. *Biomass from Sugarcane: Harvesting, Energy and Environmental*, 2nd ed.; Kluwer Academic Publishers: Piracicaba, Brazil, 2004.
36. Goldemberg, J. The Brazilian biofuels industry. *Biotechnol. Biofuels* **2008**, *1*, 1–7.
37. Smeets, E.; Junginger, M.; Faaij, A.; Walter, A.; Dolzan, P.; Turkenburg, W. The sustainability of Brazilian ethanol—An assessment of the possibilities of certified production. *Biomass Bioenergy* **2008**, *32*, 781–813.
38. Contreras, A.M.; Rosa, E.; Pérez, M.; van Langenhove, H.; Dewulf, J. Comparative life cycle assessment of four alternatives for using by-products of cane sugar production. *J. Clean. Prod.* **2009**, *17*, 772–779.
39. Gonçalves, A.R.; Benar, P.; Costa, S.M.; Ruzene, D.S.; Moriya, R.Y.; Luz, S.M.; Ferreti, L.P. Integrated processes for use of pulps and lignins obtained from sugarcane bagasse and straw: A review of recent efforts in Brazil. *Appl. Biochem. Biotechnol.* **2005**, *121–124*, 821–826.
40. Hamelinck, C.N.; van Hooijdonk, G.; Faaij, A.P. Ethanol from lignocellulosic biomass: Techno-economic performance in short-, middle- and long-term. *Biomass Bioenergy* **2005**, *28*, 384–410.
41. Pires, A.; Schechtman, R. O mapa sucroenergetico do Brasil [The sugar-energy map of Brazil]. In *De Souza e Macedo (Eds), Etanol e Bioeletricidade: A Cana-de-Açúcar no Futuro da Matriz Energética [Ethanol and Bioelectricity: Sugarcane in the Future of the Energy Matrix]*; UNICA—Brazilian Sugarcane Industry Association: São Paulo, Brazil, 2010; ISBN 978-85-63750-00-6.
42. OECD/IEA. *Sustainable Production of Second Generation Biofuels: Potentials and Perspectives in Major Economies and Developing Countries*; International Energy Agency: Paris, France, 2010.
43. Ajanovic, A.; Haas, R. Economic challenges for the future relevance of biofuels in transport in EU countries. *Energy* **2010**, *35*, 3340–3348.
44. Acquaye, A.; Wiedmann, T.; Feng, K.; Crawford, R.; Barret, J.; Kuylenstierna, J.; Duffy, A.; Koh, S.C.; Mcqueen-Mason, S. Identification of carbon hot-spots and quantification of GHG intensities in the biodiesel supply chain using hybrid LCA and structural path analysis. *Environ. Sci. Technol.* **2011**, *45*, 2471–2478.
45. Baboulet, O.; Lenzen, M. Evaluating the environmental performance of a university. *J. Clean. Prod.* **2010**, *18*, 1134–1141.
46. Arndt, C.; Garcia, A.; Tarp, F.; Thurlow, J. Poverty reduction and economic structure: Comparative path analysis for Mozambique and Vietnam. *Rev. Income Wealth* **2011**, *58*, 742–763.

47. Wiedmann, T; Suh, S; Feng, S; Kuishuang, F; Lenzen, M; Acquaye, A; Scott, K; Barrett, J. Application of hybrid cycle approaches to emerging energy technologies: The case of wind power in the UK. *Environ. Sci. Technol*. **2011**, *45*, 5900–5907.
48. Leontief, W. Environmental Repercussions and the Economic Structure: An Input-Output Approach. *Rev. Econ. Stat.* **1970**, *3*, 262–271.
49. Defourny, J. Une Approche Structurale pour l'Analyse input-output: Um Premier Bilan. *Economie Appliquée* **1982**, *35*, 203–230.
50. Lenzen, M.; Murray, J. Conceptualising Environmental Responsibility. *Ecol. Econ.* **2010**, *70*, 261–270.
51. Roberts, D. The role of households in sustaining rural economies: A structural path analysis. *Eur. Rev. Agricult. Econ.* **2005**, *32*, 393–420.
52. Wood, R.; Lenzen, M. Structural path decomposition. *Energy Econ.* **2009**, *21*, 335–341.
53. Suh, S.; Heijungs, R. Power series expansion and structural analysis for life cycle assessment. *Int. J. Life Cycle Assess.* **2007**, *12*, 381–390.
54. Lenzen, M. Structural path analysis of ecosystem network. *Ecol. Model.* **2007**, *200*, 334–342.
55. Lenzen, M. Environmentally important path, linkages and key sectors in the Australian economy. *Struct. Chang. Econ. Dyn.* **2003**, *14*, 1–34.
56. Defourny, J.; Thorbecke, E. Structural path analysis and multiplier decomposition within a social accounting matrix framework. *Econ. J.* **1984**, *94*, 111–136.
57. Martinez, H.S. *Socio-economic Assessment of Sustainable Sugarcane-Ethanol Production in Northeast Brazil, Dissertação Mestrado*; Universidade Utrecht: Utrecht, The Netherlands, 2011.