An energy analysis of first to third-generation bioethanol production in Brazil: the potential for CO_2 emissions

Flavio Numata Jr.

Department of Mechanical and Industrial Engineering,
Universidade NOVA de Lisboa – FCT&UNL,
Universidade Positivo – UP,
R. Dep. Heitor Alencar Furtado, 5000,
81280-340, Curitiba-PR, Brazil
Email: flavio.numata@up.edu.br

Abstract: First (1G), second (2G) and third-generation (3G) ethanol industrialisation produces greenhouse gas (GHG) emissions and increases carbon dioxide (CO_2) levels in the atmosphere. In this study, a life cycle assessment (LCA) concluded that hydrolysis and filtration processes have the largest environmental impact, and despite a trend of increased discharge generated by electricity related to 3G introduction, thermodynamic processes still show the highest emissions. These results demonstrate the importance of developing a strong technology base in biofuel industrialisation, predominantly due to the vast potential of 3G production, which increasingly requires higher energy consumption and more efficiency from the industrial system. As such, the aim of this paper is to assess the environmental impact caused by CO_2 emissions in 1G, 2G and 3G ethanol production.

Keywords: energy analysis; life cycle assessment; LCA; CO_2 emissions; bioethanol.

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Biographical notes: Flavio Numata Jr. is a Doctoral student at Nova University of Lisboa, Portugal. He is also a Professor advisor Industrial Engineering at Positivo University. His research focuses on environmental impacts on energy cogeneration systems in industrial manufacturing. He is author of research papers in international journals and conference proceedings.

1 Introduction

The global energy supply is highly dependent on non-renewable energy sources. Recent studies show 80% comes from fossil fuels, with approximately 36% from oil (IRENA, 2014). However, employing these sources results in air pollution (local impact), acid rain (regional impact), and greenhouse gas emissions (global impact) (CGEE, 2009). Over the past twenty years, carbon dioxide (CO_2) emissions have reached nearly 390 kg CO_2

eq./m^3, with an increase to 417 kg CO_2 eq./m3 in the last five years alone. This number has the potential to rise another 5% by 2020 (EMBRAPA, 2012). The market entry of lignocellulosic ethanol, also known as second generation (2G) ethanol, is imminent. To produce 2G, thermochemical routes convert bagasse to sugarcane lignocellulosic biomass (Borrion et al., 2012; EMBRAPA, 2012) a process which consequently increases atmospheric discharges (Dias et al., 2014). Studies show that biomass fuel industrialisation processes emit pollutants and require high energy consumption (Slade and Bauen, 2013; Yuan et al., 2015; Jong et al., 2017). These studies focus on the relationship between the energy factor required by the production system and the resulting amount of environmental impact [Slade and Bauen, (2013), p.32]. Given that energy-generated processes comprise more than 50% of CO_2 emissions (IEA, 2010), it is critical to evaluate and measure the environmental impact of biofuel production cycles and include potential CO_2 emissions as an important parameter when analysing future generations of ethanol. The most common way to do this is by implementing the life cycle assessment (LCA). This method assesses the environmental impact from products according to the mass and energy balance in their industrial processes. This study aims to measure the environmental impact of 1G, 2G, and 3G ethanol by looking at their CO2 emissions during the industrialisation phase. We use an exploratory methodology with a documentary approach to collect data, and a sensitivity analysis to identify which processes most contribute to environmental effects. We anticipate that this study will serve as a model for future studies focusing on industrial technological development and environmental protection. This method assesses the environmental impact from products according to the mass and energy balance in their industrial processes (ABNT, 2009).

2 Life cycle assessment and prospective scenarios

As far as environmental performance assessment techniques are concerned, the LCA is considered a robust and versatile tool for assessment of production systems in prospective scenarios (Jacquemin et al., 2011). That being said, assessment results are an estimate and may present inaccuracies in production data projections, applied technologies, or local specificities. In order to evaluate these deviations, this study performed a sensitivity analysis (SA). This technique simulates data through the application of different parameters to verify the production and environmental behaviour of a given technological structure. The SA checks the influence of one parameter (independent variable) against another (dependent variable), and demonstrates its interference in the final result (Heijungs and Huijbregts, 2004).

It is vital to understand how innovation and new technologies in production systems contribute to inventory systematisation. To do so, studies should consider (Kulay and Seo, 2006):

- technologies with the highest frequency of application in the sector
- technologies with the largest productive scales
- technologies with a more rudimentary operation
- incoming technologies.

Technology is a crucial factor when assessing future generations of ethanol. It determines the materials and energy flows used in the processes and analyses the environmental performance of the production system. In this respect, the SA is an important tool, allowing studies to simulate the production potential of distillation plants, identify contributions of process variables, and estimate environmental effects.

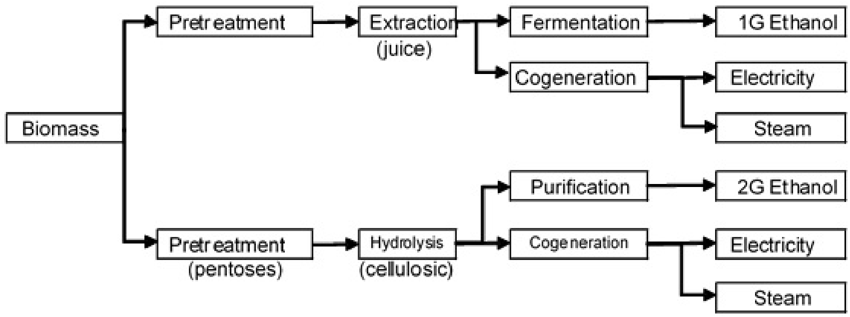
3 Methodology and study structure

This study used the LCA to assess environmental impacts and the Intergovernmental Panel on Climate Change (IPCC) guidelines (2006) to measure CO_2 emissions derived from ethanol industrialisation processes. Energy and biomass resources representing elementary flows were obtained through research reports and a literature review of life cycle inventory (LCI) data. Energy data from the industrialisation processes was calculated by technology used to measure emissions. The overall scope of this study considers ethanol production up to 2050, including future generations of Brazilian ethanol. Data collection takes into account data from the Ecoinvent v.2 (2007) in relation to temporal, geographical, and technological dimensions:

- For the temporal scope, we included the target dates for 2G and 3G laid out in studies conducted by the Energy Research Company of the Brazilian Ministry of Mines and Energy (EPE), the Center for Advanced Studies (CGEE), and the Institute of Applied Economic Research (IPEA) (2015), a Brazilian government-led research organisation.
- For the geographical scope, we looked at 1G and 2G data from Brazilian studies and 3G data primarily from European studies, which account for most of the world studies in the subject. The main sources of this research are CETESB (2011), Dias et al. (2013), EMBRAPA (2012), IRENA (2014), Passell et al. (2013) and Quinn et al. (2014).
- For the technological scope, 2G data was drawn from the study of Brazil's National Bioethanol Science and Technology Laboratory (CTBE) conducted by Dias et al. (2013) as well as other studies carried out by Borrion et al. (2012), Scotia Capital (2010), Pirilla (2012) and Wiloso et al. (2012). 3G data was drawn from studies conducted by Derminbas (2011), Milledge and Heaven (2014), Parvatker (2013), Passell et al. (2013), Brentner et al. (2011), Yuan et al. (2015), Batan et al. (2010), Clarens et al. (2010), Dias et al. (2014), Quinn et al. (2014) and Peng and Zhou (2014).

Data collection was carried out according to NBR ISO 14044:2009 requirements and LCA principles. Figure 1 shows the reference flows and their data on 1G, 2G, and 3G bioethanol direct flows.

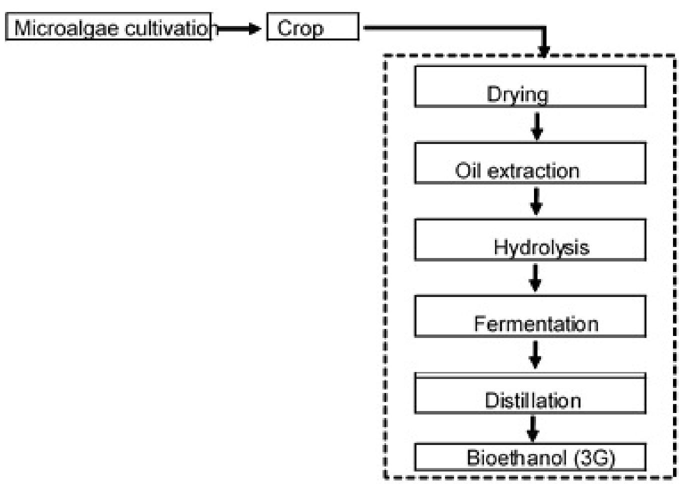
Figure 1 1G and 2G ethanol system



Source: Adapted from Dias et al. (2014)

Figure 2 presents the 3G ethanol industrialisation system delineated by the dotted line.

Figure 2 3G ethanol system



The system border is 'gate to gate'. The functional unit corresponds to 1kg of bioethanol produced, and emissions are reported in kg units of carbon dioxide equivalent (kg CO_2 eq.). The evaluation is based on Centre for Environmental Studies (CML) (2000), a life cycle impact assessment (LCIA) methodology that considers the effects caused by territorial, temporal, and technological factors in the processes (ISO, 1998; JRC, 2010).

4 1G, 2G and 3G ethanol industrialisation

4.1 1G and 2G ethanol

Turbine-driven industrial systems are more efficient than boilers due to their superior steam generation rate and lower emission of particulates, such as carbon monoxide, carbon dioxide, and nitrogen oxide (CGEE, 2009). Additionally, turbines can operate at higher temperatures and pressures, producing energy without consuming the steam from the industrial process which also needed to generate electricity in cogeneration processes.

In topping (inbound) systems, fuel is burned to produce mechanical energy and then generate electricity. In the bottoming (outbound) system, rejected energy from industrial processes is converted into steam to fuel the turbogenerators that operate the manufacturing devices. In Brazil, the systems, or their cogeneration technological alternatives, are (MME, 2014):

- cogeneration with boilers
- cogeneration with back pressure turbines
- cogeneration with condensation and extraction turbines
- cogeneration with combined-cycle turbines.

Systems using boilers and back pressure turbines are considered conventional and are more common in Brazilian distilleries. This model presents a lower performance capacity when compared to other systems, with 55% efficiency in boilers and 34% in turbines (Correa Neto and Ramon, 2002). The topping operation model utilises extraction and condensation turbines and combines heating devices and condensers to reduce steam consumption and optimise processes. The efficiency rate in this cycle is 84.5% in the boilers and 75% in the turbines. The combined cycle uses gas and steam turbines for the generators and, due to the high temperature of gases (energy content), can reach 50 to 70% efficiency (Oddone, 2001). This operating efficiency is related to the type of organic matter in the biomass. Bagasse energy potential is mainly associated with the degree of moisture because the residual sugar content is relatively low (Innocente, 2011). For instance, for each average reduction of 10% moisture, the lower calorific value (LCV) increases by approximately 20%. As such, it turns out that LCV is an important factor in identifying the input energy potential. For example, the bagasse LCV is 7.5 MJ/kg with 50% moisture content or 15.5 MJ/kg for 8% moisture (Seabra and Macedo, 2011), and the use of straw results in a 12.8 MJ/kg LCV, approximately 70% higher than the sugarcane bagasse LCV. For 2G ethanol, a complex process of cellulose hydrolysis and glucose fermentation is carried out in separate reactors (SHF – separate hydrolysis and fermentation). Another option is biomass gasification. Since this process involves combined cycles of gas and steam turbines, it is better known as the biomass integrated gasification and gas turbine combined cycle (BIG/GT-CC) (Oliveira et al., 2014). Here, the bagasse is subject to gases in high temperatures, mainly CO_2, H_2, CO and steam (Garcia and Sperling, 2014). This generated gas burns in gas turbines and is then used to fuel steam turbines in combined cycles to generate electricity. Gasification may use different technological routes, depending on the type of biomass being processed, the scale, and the manufacturing product (Patzek and Pimentel, 2005).

4.2 3G ethanol

The first phase of bioethanol production corresponds to algae cultivation. The production system can be housed in open environments, known as raceway or open-air systems (Brennan and Owende, 2011), or closed and hybrid ones, called photobioreactors (Pulz, 2001). Each type of system applies different processes that require different energy needs. Open environments have a consumption rate of 60% electricity and 40%

chemicals (FAO, 2008). Conversely, closed systems have a consumption rate of 45% electricity and 55% chemical inputs. In the recovery phase, biomass preparation can be performed with varied processes, such as flocculation, centrifugation, filtration, ultrafiltration, or flotation (Harun et al., 2010; Kadam, 2011). Biomass separation from its culture medium is carried out specifically by flocculation, flotation, and sedimentation. Drying presents an average yield of 95% (Kouhia et al., 2015; Lardon et al., 2009) and 25% of lipid content (Chaudhary et al., 2014; Ou et al., 2013). Then, filtration and centrifugation are used to thicken the matter. Centrifugation requires 0.15 MJ/kg (Kadam, 2011; Yuan et al., 2015) and drying requires 2.6 MJ/kg (Kadam, 2011). Drying can be executed by means of solar exposure or with spraying or lyophilisation techniques, the latter guaranteeing higher productivity (Brennan and Owende, 2011). Due to these characteristics, this phase presents the highest concentration of limiting factors in the entire algae production chain (Dragone et al., 2010). In the cell rupture phase, sugar extraction may be initiated when preparing the biomass. The methods for oil extraction from algae are (Kouhia et al., 2015):

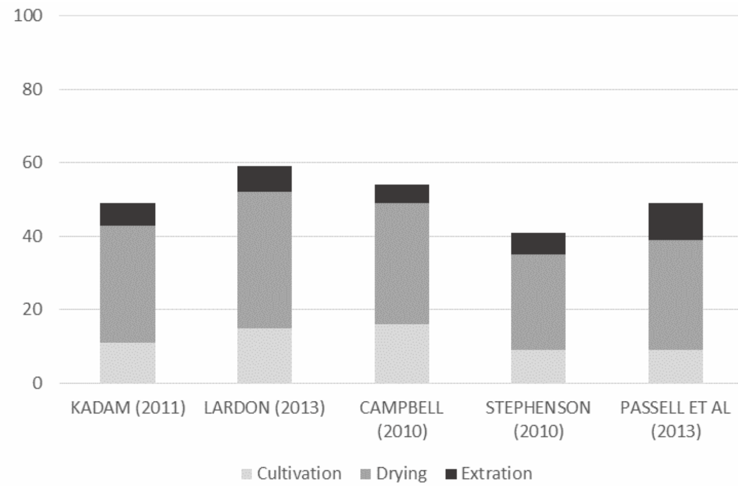
- pressing
- solvent extraction
- supercritical fluid extraction
- enzymatic extraction
- osmotic shock.

The extraction can be performed in two ways. Mechanical action uses presses to compress the biomass. Chemical action uses substances consisting primarily of hexane (Govindarajan et al., 2009); hexane-methanol, for example, is employed in 98% of the cases. The chemical process has a wide application with oxidation to generate cell rupture and lipid extraction. The supercritical extraction process uses high thermodynamic tensions for cell rupture and oil extraction, making it one of the fastest and most efficient extraction processes (Harun et al., 2010). The final phase includes the fermentation of hexoses or pentoses, followed by distillation in order to obtain bioethanol.

These production phases consume different amounts of energy, according to the Net Energy Ratio (NER), an energy indicator for electricity production that demonstrates energy demand per bioethanol industrialisation phase (Herbst et al., 2012; Kadam, 2011; Lardon, 2009; Campbell et al., 2011; Stephenson et al., 2010; Passell, 2010).

Research shows a higher energy consumption rate in the biomass drying stages, corresponding to more than 50% of total energy consumption. On average, the cultivation phase is half of this value. The oil extraction phase tends to have a low consumption rate thanks to a combination of hydrolysis process with bio-reactions in the biomass cell composition (Yuan et al., 2015). Energy consumption varies between 0.39 MJ/kg (Collet et al., 2013), 0.47 MJ/kg (Brentner et al., 2011), and 0.59 MJ/kg (Yuan et al., 2015). Hydrolysis is performed by enzymatic or acidic action, with use of chemical reagents for saccharification, and then the fermentation of sugars (glucose) is carried out by microorganisms (Demirbas, 2011). The whole fermentation process generates diluted alcohol with a concentration of 10% to 15% ethanol. This product must be concentrated and distillation-purified to remove water and other impurities. Finally, concentrated ethanol is recovered and condensed in liquid form, transforming into biofuel. Overall, these processes consume approximately 10 MJ/kg of steam and 3.5 MJ/kg of electricity (Kouhia et al., 2015).

Figure 3 Energy consumption rate in production phases (%)



Source: Kadam (2011), Lardon (2009), Campbell et al. (2011), Stephenson et al. (2010) and Passell et al. (2013)

5 Outline of environmental impact metrics

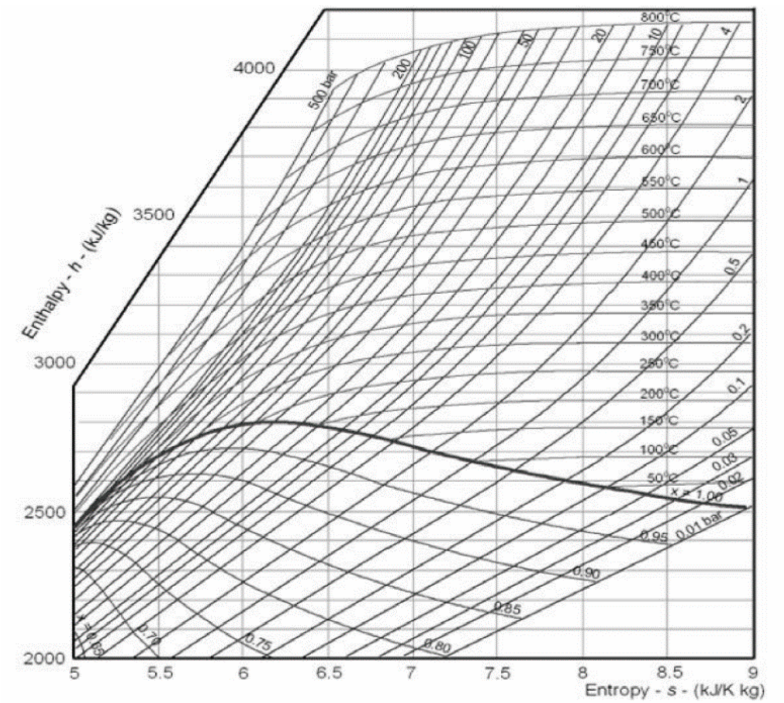
5.1 Ethanol (1G and 2G)

As we can see, the bioethanol industrialisation process, from drying to purification, requires significant energy consumption. Energy consumption (*E*) is associated with the production operations (*P*) according to the value associated with the flow of each operation process (*i*), in the $Ei = f(Pi)$ function. Considering this factor and its environmental emission coefficient (*c*), the environmental impact value (*I*) can be determined by:

$$Ii = Ei \cdot ci \tag{1}$$

This corollary follows the conceptual principles of de Haes and Lindeijer (2002), where the equation aimed to identify the relationship between production, energy, and the production technology. This principle is valid because different technologies may have different impact intensities per produced energy unit. For instance, 1G ethanol has different contributions than 2G because it processes sugarcane components with different operations in its production cycle (Borrion et al., 2012; Ojeda et al., 2011; Dias et al., 2014). Steam flow generated from the processes acts as fuel for the plant's devices, and it is important to observe its use in turbines for electricity and ethanol production. Considering thermodynamics conceptual premises of 'work for operation', Figure 4 shows the process parameters through Mollier's diagram [Hinrichs and Kleinbach, (2003), p.40].

Figure 4 Mollier's diagram



Source: Engineering Toolbox (2003)

The energy present in the steam, known as enthalpy, is related to the pressure and temperature established in each industrial system operation. Based on the first law of thermodynamics, this relationship expresses the rate of change of enthalpy with heat transfer between operations (Hinrichs and Kleinbach, 2003). This thermal variation along with the efficiency of the devices allows for the identification of the system mass flow rate. Mollier's diagram shows that the greater the reduction of steam enthalpy, the greater the capacity of electricity generation. This is a result of the moisture content in bagasse which allows for reduction throughout the process, thereby increasing its calorific value. As such, the drier the biomass, the higher its energy within the compound, resulting in a greater LCV (Albarelli, 2013). The energy variation, known as process enthalpy, is related to fuel consumption (Balestieri, 2002):

$$Fuel\ consumption = \frac{fuel\ mass}{energy} \tag{2}$$

As seen above, more energy requires lower fuel consumption, favouring the processing performance and reducing environmental effects. Operation conditions demonstrate that the pressure rise with controlled temperature increases the process efficiency up to a certain operational limit (Cavalett et al., 2011). Meanwhile, pressures and temperatures above 70 bar or 550°C do not contribute significantly to the reduction of steam consumption (Dias et al., 2012a). This is a notable result due to the potential mitigation of environmental impacts through the reduction of gases emission offered by systems of gas and steam combined cycles. According to a study by Dias et al. (2013), high pressure increases, above 50 bar, result in lower bagasse consumption for steam production and lower energy requirements for the processes (Milanez et al., 2014). Other measures that improve a plant's energy efficiency are broth treatment, alcoholic fermentation, distillation, gasification, and steam distribution among devices (Correa Neto and Ramon, 2002). Severe pressure and temperature conditions are the most likely to be adopted in future operations using lignocellulosic biomass as feedstock, resulting in an optimised ethanol and cogeneration production (Conab, 2011). Pressure and temperature data differ according to industrial process technology and installed thermochemical route. This study considered the average data from industrial operations within this context. The main parameters of the processes are the working temperature and pressure, data that allows us to check the amount of energy required in the industrial phase. These parameters are based on research and simulations conducted by Leal and Macedo (2004), Macedo and Nogueira (2004), CGEE (2009), Ensinas et al. (2009), Seabra (2008), Pelegrini and de Oliveira (2011), Albarelli (2013), Dias et al. (2012a, 2013) and Oliveira et al. (2014). These data can also represent the processes and portray the working conditions the plant will use to format the inventoried data in each future period for analysis. Table 1 groups the projection of most used data in the simulations held in plants:

Table 1 Projection of thermodynamic parameters per ethanol production industrial devices

	2020	*2030*	*2040*	*2050*
	Working temperature (°C)			
Boilers	400	300	350	-
Backpressure turbines	470	400	480	480
Condensation-extraction turbines	400	500	480	520
Combined-cycles turbines	-	520	500	480
	Working pressure (bar)			
Boilers	22	20	25	-
Backpressure turbines	22	50	65	65
Condensation-extraction turbines	25	42	80	82
Combined-cycles turbines	-	20	82	90
	Steam consumption (kg/TC)			
Boilers	500	455	360	-
Backpressure turbines	500	425	505	500
Condensation-extraction turbines	679	400	350	340
Combined-cycles turbines	-	580	350	280

Source: Leal and Macedo (2004), Macedo and Nogueira (2004), CGEE (2009), Ensinas et al. (2009), Seabra (2008), Albarelli (2013), Dias et al. (2012a, 2013), and Oliveira et al. (2014)

The industrialisation capacity is directly linked to the biomass supply. Table 2 projects the average values for use in the data inventory.

Table 2 Biomass supply for industrialisation

Biomass	*2020*	*2030*	*2040*	*2050*
Bagasse (million kg)	114,110.080	131,591.740	151,751.600	175,000.000
Straw (million kg)	57,055.040	65,795.870	75,875.800	87,500.000

Source: Adapted from EPE (2014), CTC (2017), Silva et al. (2012), Hassuani et al. (2005) and Walter and Ensinas (2010)

Data consider sugarcane estimated production in the proportion of 25% in biomass form (EPE, 2014), with a generation of 140 kg in bagasse or straw per sugarcane ton (CTC, 2017; Silva et al., 2012), and 50% of the straw volume for processing plants (Dias et al., 2012b; Hassuani et al., 2005; Walter and Ensinas, 2010). Biomass projection and technological potential play important roles in determining how to reduce energy consumption and its interference in the future. For instance, adding straw and introducing the hydrolysis process (acid and enzymatic) increases electricity generation and bioethanol production. A number of additional processes geared toward efficiency are also in the works, such as the elimination of bagasse excess (full use), reduction of steam consumption, substantial increase of working pressure in turbines, and optimisation of industrial processes in sugarcane washing, fermentation, and filter cake loss (CGEE, 2009). Overall, the aim is to increase energy productivity by approximately 30% in the next decade (Oliveira et al., 2014). Studies on 1G and 2G integration have shown that doubling the working pressure in boilers or turbines reduces steam consumption by 5%, increases ethanol productivity by 43%, and generates energy surpluses (Dias et al., 2013). It is necessary to measure how much energy is supplied by the raw material being processed. To determine the amount of biomass consumed during these processes, the following data should be considered:

- contribution rate of raw materials for productive options
- variation of process enthalpy
- LCV of the substance
- performance of the system mechanical unit (boiler/turbine).

Biomass is used for electricity generation (46.3%) and steam production (53.7%), which covers steam generation as well as the activation of distillery devices (mechanical and thermal energy) (Dantas, 2010; Santos, 2012; Torquato and Ramos, 2013). The productive fraction makes it possible to pinpoint the exact emission generated for electricity and ethanol production. Ultimately, the type of discharge depends on the type of process used at the plant, and the LCV varies according to type of product being processed. In this study, the straw and sugarcane bagasse have the following energy loads:

- bagasse LCV: 7,536 KJ/kg (Conama, 2011; UNICA, 2009)
- straw LCV: 12,811 KJ/kg (Lamonica, 2005; UNICA, 2009).

The potential energy of the process, in the form of enthalpy, fluctuates according to the type of mechanical system installed. Consistent with the anticipated industrial system operational parameters, the efficiency rate should reach the average values (COGEN Europe, 2001) presented in Table 3.

Table 3 Thermodynamic systems efficiency

Technological systems	*2020*	*2030*	*2040*	*2050*
Backpressure turbines	70%	70%	70%	79%
Condensation-extraction turbines	73%	73%	73%	73%
Combined-cycles turbines	79%	79%	79%	79%

Source: Oddone (2001), Chohfi (2004), Barja (2006), Dantas (2010), Walter and Ensinas (2010), Dias et al. (2013) and Lobo (2013)

Table 4 presents the weighted average yield (R) according to their rate of participation (P) with the technology in distillation plants and their usage period:

Table 4 Weighted yield

Technological systems participation (P), weighted yield (R)	*2020*		*2030*		*2040*		*2050*	
	P	*R*	*P*	*R*	*P*	*R*	*P*	*R*
Boilers	2%	60%	0%	0%	0%	0%	0%	0%
Backpressure turbines	69%	70%	61%	70%	56%	70%	50%	79%
Condensation-extraction turbines	24%	73%	26%	73%	28%	73%	31%	73%
Combined-cycles turbines	5%	79%	13%	79%	15%	79%	19%	79%
Weighted yield	69.66%		71.62%		72.24%		77.14%	

Source: Leal and Macedo (2004), Macedo and Nogueira (2004), CGEE (2009), Ensinas et al. (2009), Seabra (2008), Albarelli (2013), Dias et al. (2012a, 2013) and Oliveira et al. (2014)

The data represent operational technological systems and will therefore be categorised by time period. Analysing these observations through the lens of thermodynamic principles and technological factors, the volume of the resource under conversion (mass flow) in the system is calculated by Shapiro (1996, adapted):

$$M = \frac{B \cdot p_v \cdot PCI \cdot n}{\Delta H} \quad (3)$$

Data:

- M – amount of steam mass consumed (kg)
- B – amount of biomass (kg)
- p_v – contribution coefficient for steam generation: 53.7% (Dantas, 2010; Santos, 2012; Torquato and Ramos, 2013)
- LCV – lower calorific value of biomass (kJ/kg)
- ΔH – enthalpy variation in working pressure/temperature in the mechanical unit (kJ/kg.year)
- n – efficiency of the device (upon admission).

Data correlation makes it possible to evaluate future scenarios, taking into account the process and input conditions according to each technological route. Mass flow can be used for electricity cogeneration or steam generation for ethanol production. Fuel conversion requires steam energy to operate the equipment, and results show the specific consumption under these conditions.

The environmental load is calculated considering the relation among mass flow, the specific steam/fuel consumption, and the related emission factors:

$$E_{cb} = M \cdot (C_{ev})^{-1} \cdot F_{ev} \tag{4}$$

where

E_{cb} emissions from biomass conversion into fuel

M amount of steam mass consumed (kg) according to equation (3)

p_e contribution coefficient for electricity generation: 46.3% (Dantas, 2010; Santos, 2012; Torquato and Ramos, 2013)

C_{ev} 14.69 kg steam/l ethanol (Camargo et al., 1990; Correa Neto and Ramon, 2002)

F_{ev} 0.937 kg CO_2/l ethanol (Ometto, 2005).

On top of the emissions generated in conversion processes and fuel transformation, additional discharges are caused by cogeneration. Electricity generation requires operation with power converters, and it is necessary to use the specific amount of electricity consumed by the resource under processing. The cogeneration emissions are calculated using equation (5).

$$E_{el} = M \cdot C_e \cdot F_{el} \tag{5}$$

where

E_{el} emissions from biomass conversion into electricity

C_{el} 0.012 kWh/kg (Macedo, 2004)

F_{el} 0.745 kg CO_2/kWh (adapted from Gabi, 2007; Medeiros et al., 2013).

Taking into account data presented for bagasse, the emissions generated by bioethanol production and electricity are shown in Table 5.

Table 5 Generated emissions in bioethanol production and bagasse cogeneration

Bagasse processing (kg CO_2)	*2020*	*2030*	*2040*	*2050*
Bioethanol production emission	1.003140	1.043387	1.108501	1.172278
Electricity generation emission	0.021254	0.020869	0.016760	0.017327

Table 6 presents projected emissions for straw.

Table 6 emissions generated in bioethanol production and straw cogeneration

Straw processing (kg CO_2)	*2020*	*2030*	*2040*	*2050*
Bioethanol production emission	0.250224	0.245688	0.246643	0.254985
Electricity generation emission	0.036574	0.034914	0.035043	0.035280

Data on the future production of biomass underwent a sensitivity analysis with regards to the average estimate of the energy scenario. The records are based on prospective EPE reports from the Brazilian Ministry of Mines and Energy, and production data, such as specific substance use or enthalpy, were accounted for in terms of industrial-technological infrastructure. Emission factors come from international databases, such as Ecoinvent or GABI, and correspond to the parameters of past studies. In certain situations, data was pulled from reports on global warming from the IPCC or TRACI (Tool for the Reduction and Assessment of Chemical and other Environmental Impacts).

4.2 3G ethanol

3G ethanol industrialisation processes are drying, hydrolysis, fermentation, and filtration. Biomass drying is the preparatory step. Hydrolysis uses a chemical or mechanical route to alter the biomass cellulosic structure in preparation for cellular rupture. From the resulting hydrolysate, fermentation for cellulosic action is carried out through chemical reactions. In the last step, water is separated from ethanol through filtration. In each step, energy is the key factor for production efficiency and environmental performance. The processes require high electrical charges from different sources that vary depending on the job being carried out, emphasising the importance of the energy in this production system. Therefore, energy can be used as the process evaluation vector, evaluating the environmental performance of each operation and characterising the manufacturing technology (Luo et al., 2010). This condition is important because current technology may interfere with the results. In all conditions, we follow principles of the first law of thermodynamics that are suitable for measurement in prospective scenarios, such the adiabatic system of mass conservation. The first step is biomass preparation. This involves two processes: centrifugation to separate waste and water from the biomass, and biomass heat drying. The required energy flow is considered for each process, and the environmental effects are measured as follows:

$$Epr = \sum\nolimits_{i=1}^{n} energy\ \ flow \cdot M_{algae} \cdot F_{emission} \tag{6}$$

Equation (6) presents the overall corollary of the environmental impact metric, which can be decomposed for each step of the industrialisation process. Equation (7) measures the impact of the biomass preparation phase including centrifugation and drying:

$$Epr = \left(0.15 \cdot M_{algae} \cdot F_{emission\ el}\right) + \left(2.6 \cdot M_{algae} \cdot F_{emission\ vp}\right) \tag{7}$$

- Epr – environmental effects on biomass preparation
- M_{algae} – algae biomass volume (kg)
- $F_{emission\ el}$ – emission energy factor in electricity form (kg CO_2 equiv/kWh)
- $F_{emission\ vp}$ – emission energy factor in steam form (kg CO_2 equiv/MJ).

The average coefficient of electricity consumption per algae unit mass from flotation or centrifugation processes is 0.15 kWh/kg (Parvatker, 2013). The average coefficient of energy consumption in steam form per algae unit mass in the drying process is 2.6 MJ/kg (Passell et al., 2013).

As observed, the algae emission factors may assume different values. Research on LCA shows gaps in reference data in the experimental phase of this biomass source (IEA, 2010; Slade and Bauen, 2013). However, by systematising data according to variable flow, we can configure the evaluation scenario as an attempt to solve this limitation. In this scenario, it is important to consider production factors that act indirectly on the resource under conversion, such as infrastructure and technology (REN21, 2013). Evaluating the biomass molecular structure with manufacturing technology allows for a more consistent measurement of the emissions.

Thus, the emission factor is related to the molecular composition through its carbon balance (CB):

$$CB = \left(M_{CO2} / Q_c\right) \cdot F_{em} \tag{8}$$

CB carbon balance;

M_{CO2} carbon dioxide molecular mass

Q_c carbon molecular weight

F_{en} ethanol molecular mass fraction per carbon molar unit

Molecular mass is calculated using the chemical formula of ethanol C_2H_5OH related to the participation fraction per carbon unit:

- $M_{CO2} = 46$ g
- $CB = 2.001$ g.

Measuring the emission charge according to the ratio between CB and the specific energy consumption per functional unit, we get:

$$F_{emission} = CB_{CO2} / C_{el} \tag{9}$$

- $F_{emission}$ – emission factor in electrical processes
- C_{el} – average electricity consumption coefficient per algae mass unit equivalent to 21.9 MJ/kg algae (Meyer et al., 2010).

$$F_{emission} = 0.00050 \text{ kg } CO_2$$

The same principle is applied to determine the emission factor for processes involving thermal energy consumption:

$$F_{emission} = CB_{CO2} / C_{vp} \tag{10}$$

- $F_{emission}$ – emission factor in thermodynamic processes
- C_{el} – average electricity consumption coefficient per algae mass unit from flotation and centrifugation processes equivalent to 0.15 kWh/kg (Parvatker, 2013).

$$F_{emission} = 0.00200 \text{ kg } CO_2$$

The oil extraction requires a mechanical compression device that consumes electricity. The average energy consumption of hydrolysis proposed by Brentner et al. (2011) is 0.47 MJ/kg, according to surveys in Colet et al. (2013) and Yuan et al. (2015). The next step is hydrolysis. This can be carried out in either an acidic or enzymatic medium, the latter consuming thermodynamic energy. The use of enzymes is more productive, but its processing is slower than acid hydrolysis because it requires previous treatments (Lynd et al., 2002) using H_2SO_4, HNO_3, or HCl acids.

Following cell rupture, the oil extraction process consumes approximately 2.45 MJ/kg (Azeredo, 2013). Emissions can be measured by the same principle used in equation (9), considering:

$$Ehd = \left(0.47 \cdot M_{algae} \cdot F_{emission\ vp}\right) + \left(2.45 \cdot M_{algae} \cdot F_{emission\ el}\right) \tag{11}$$

- Ehd – hydrolysis emission (kg CO_2 equiv)
- M_{alage} – algae biomass volume (in dry mass) (kg)
- $F_{emission\ st}$ – energy emission factor in steam form (kg CO_2 equiv/MJ)
- $F_{emission\ el}$ –energy emission factor in electricity (kg CO_2 equiv/kWh).

The average coefficient of energy consumption in steam form per algae unit mass is 0.47 MJ/kg (Brentner et al., 2011).

The average coefficient of energy consumption in electricity form per algae unit mass is 2.45 MJ/kg (Azeredo, 2013).

The next step is fermentation. Fermentation is the process of bioethanol generation, which involves nutrients, water, and microorganisms. Due to its high anaerobic and productive potential, the most commonly-used yeast in industrialisation is *Saccharomyces cerevisiae* (Markou et al., 2013). Bioreactors are also used in the process to intensify chemical reactions. The average energy consumption of booster pumps and heating is 4.21×10^{-3} MJ/kg (Ferreira et al., 2012).

The final step is filtration. Here, water is separated from the produced ethanol, with a specific consumption of 0.0067 kWh/kg (Luo et al., 2010).

Emissions are measured by the relationship of energy consumption and the applied mass of the biomass:

$$Efm = \left(0.00421 \cdot M_{algae} \cdot F_{emission\ vp}\right) + \left(0.0067 \cdot M_{algae} \cdot F_{emission\ el}\right) \tag{12}$$

- Efm – fermentation/filtration emission (kg CO_2 equiv)
- M_{algae} – algae biomass volume (kg)
- $F_{emission\ st}$ – energy emission factor in steam form (kg CO_2 equiv/MJ)
- $F_{emission\ el}$ – energy emission factor in electricity form (kg CO_2 equiv/kWh).

The average energy consumption coefficient in steam form per algae mass unit is 0.00421 MJ/kg (Ferreira et al., 2012; Kouhia et al., 2015).

The average energy consumption coefficient in electricity form per algae mass unit is 0.0067 kWh/kg (Luo et al., 2010).

Each process emission was calculated based on the metrics presented above. Table 7 presents these results.

Table 7 Processes emissions (UF)

Emissions in algae industrialisation processes (kg CO_2 eq)	*2050*
Centrifugation	0.003379
Drying	0.000195
Hydrolysis	0.001078
Oil extraction	0.000207
Fermentation	0.120387
Filtration	0.075646

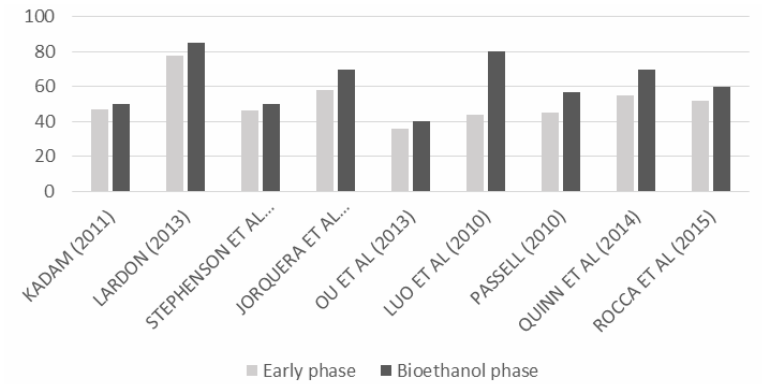
5 Results and discussion

The metric composition illustrates the interference of dynamic factors on the process flows, such as:

- usage type of input resource (biomass)
- workloads (manufacturing operation parameters)
- processes equipment capacity (machinery efficiency)
- relation of technological infrastructure with the evaluation period.

Each of the aforementioned elements contributes in a different way and intensity to environmental performance. Biomass contribution is measured in thermodynamic workloads. In terms of the source of raw material, this contribution is mainly related to the water content in its molecular composition. This context confirms the importance of considering specific industrialisation data and biomass composition for environmental evaluation, which can reach a variation of up to 15% of the emissions generated between ethanol production and electricity cogeneration (Macedo and Seabra, 2010; Cavalett et al., 2011; Dias et al., 2012b). There is no competition between ethanol production and electricity cogeneration, and it is appropriate to optimise the system at a balanced productivity level between production and cogeneration in the system. Avoided emissions increase with the thermoelectric efficiency level of the systems. The fermentation process presents the highest level of emissions in all stages of industrialisation, corroborating data from the EMPA report (2007). Subsequently, filtration presents 37% less discharges than fermentation, while other processes, such as hydrolysis and oil extraction, have a very low emission load, representing less than 1% of the total contribution. These results are similar to those presented by Kadam (2011), Lardon (2009), Stephenson et al. (2010), Jorquera et al. (2010), Ou et al. (2013), Luo et al. (2010), Passell et al. (2013), Quinn et al. (2014) and Rocca et al. (2015). These studies assessed the impacts in the beginning phase (biomass preparation) and in the bioethanol phase (hydrolysis and fermentation). Figure 5 compares these results:

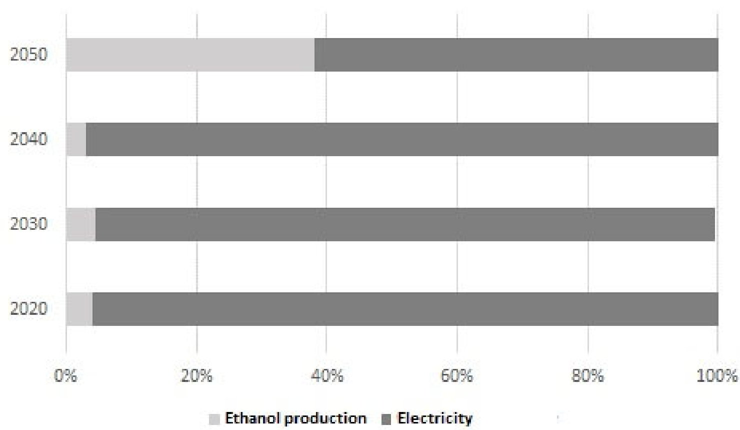
Figure 5 Comparison among main emission processes (%)



Source: Rocca et al. (2015)

Fermentation processes are derived from chemical reactions that act under specific pressure and temperature conditions combined with microorganisms, which generate H_2 and CO_2 discharges. Disparity in drying emissions depends on the algae cultivation method (open or closed systems) because different systems interact differently in moisture elimination (Slade and Bauen, 2013). The higher the aqueous content, the higher the discharge rate and equipment energy consumption, resulting in an overall increase in emission generation. As shown in Figure 6, thermodynamic energy generates a higher emission rate compared to other energy sources.

Graph 3 Emissions in kg of CO_2 eq. per energy source



The industrialisation phase showed a higher consumption of thermodynamic energy and a higher emission rate than processes that use electricity. The heating and biomass preparation phases have the highest energy consumption: approximately 28% in steam and 13% in electricity (Borkowski et al., 2012). Nevertheless, this is not a constant or regular condition in manufacturing processing since processes that use steam can sequester carbon through bioreactors drainage (Luo et al., 2010). During conversion stages, the content of biomass lipid concentration captures carbon, and it may also interfere with the emission rates (Ou et al., 2013; Rocca et al., 2015). The thermal integration between production and cogeneration optimises productivity with higher ethanol production and higher generated biomass volume. The choice of the processing technology route also interferes with the efficiency of the system's thermoelectric cycle. Furthermore, the high production efficiency of thermodynamic energy sources leads to less environmental interference, averaging 70% to 90% compared to 20% to 40% for electricity (IEA, 2010).

Algae production does not directly compete for territorial areas due to its hydric cultivation. Its lower production cycle, especially when compared to sugarcane, is another reason to use of algae as a biomass source. In light of these results, 3G has great potential for energy production and the environmental conservation. The MME and the CGEE feature 3G in the energy and technology portfolio for its socio-environmental sustainability. They predict wide-ranging use within the next 10 years and commercialisation in Brazil by 2050 [CGEE, (2009), p.170]. In this sense, the demand for bioethanol processing will increase, requiring continued technological development in the working infrastructure in order to minimise future environmental impacts.

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