Diversifying the technological strategies for recovering bioenergy from the two-phase anaerobic digestion of sugarcane vinasse: An integrated techno-economic and environmental approach

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ABSTRACT

Keywords:
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Technical, economic and environmental aspects of implementing two-phase anaerobic digestion (AD), i.e., acidogenic + methanogenic systems, in sugarcane biorefineries for the treatment of vinasse were assessed based on different strategies to using the hydrogen-rich biogas (biogas-H_2) generated via acidogenesis. Phase separation greatly enhanced the bioenergy recovered from vinasse AD compared with single-phase systems (methanogenic phase exclusively). The best results for generating electric energy were observed in combined cycle-based power plants that utilized biohythane (10.8 MW + 5.5 MW for the harvest and inter-harvest, respectively), which is the gaseous biofuel from blending biogas-H_2 with the methane-rich stream from the methanogenic phase (biogas-CH_4). Moreover, the results of this study indicated that scaling up two-phase AD systems is economically feasible for the treatment of sugarcane vinasse (net present value = USD 208.58–219.86 million) because a better or equivalent economic performance was attained compared with single-phase processes. Optimizing the alkalinization of methanogenic reactors strongly affected both the economic and environmental performance of the process, with better results observed with the use of low sodium hydroxide dosages (4 g NaOH kg^{-1}COD). In summary, our results highlighted that two-phase biodigestion may enhance energy production from vinasse by 20–30% without impairing the profitability of the biorefinery and could lead to slight improvements in the environmental performance of the ethanol production chain via the use of an optimized alkalinization strategy.

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1. Introduction

The concept of biorefining has recently attracted great interest in the agro-industrial sector because of the potential to expand the exploitation of raw materials by simultaneously producing different types of value-added products and/or recovering energy directly from residues [1]. Sugarcane-based sugar and ethanol plants are important examples of biorefineries based on the conversion of feedstock into sugar, ethanol, and even electricity because burning bagasse and straw in boilers may result in surplus electric energy sold to the grid [2]. Despite the efficient utilization of sugarcane in such facilities, a considerable fraction of the sugarcane energy content remains in the vinasse as residual organic matter from fermentation. Most of the organic content of vinasse is composed of easily degradable compounds, such as unconverted organic matter (residual fractions of reducing sugars and sucrose), compounds formed in competing fermentative metabolic pathways (glycerol and organic acids), and unrecovered fractions of ethanol [3].

In Brazil, sugarcane vinasse is commonly returned to the sugarcane fields via fertirrigation to recycle water and nutrients, predominantly potassium [4], to the crop. Although studies have associated beneficial results with fertirrigation [5,6], including reduced expenses from inorganic fertilizers, disposing vinasse on land may generate several negative impacts for the soil-water-plant system over the long term [4,7]. The biorefinery concept indicates that the direct land application of vinasse reflects the underuse of a highly energetic raw material because biotechnological approaches are potentially suitable for the processing of such wastewater, particularly via anaerobic processes.

Reference studies highlight the suitability of anaerobic digestion (AD) or biodigestion as the core technology for the treatment of vinasse, and they primarily focus on the reduction of organic polluting loads with bioenergy recovery through biogas production in single-phase anaerobic digesters [8–12]. Recently, research groups have also investigated the suitability of biohydrogen production from such wastewater [13–15] and proposed the operation of an acidogenic phase prior to methanogenesis. The high levels of residual sugars from vinasse may be directly fermented into hydrogen (H_2) and volatile fatty acids (VFAs) by acidogenic bacteria, which greatly increases the resource recovery efficiency in sugarcane biorefineries. In short, phase separation may be directed to the enhanced production of value-added biochemicals, which is primarily based on the recovery of VFAs, whereas bioenergy generation is maximized when the acidified effluent is applied to subsequent methanogenic reactors [1,16]. Particularly, phase separation provides a range of important benefits over methanogenic systems based on the marked improvements in the biodegradability of the wastewaters [17]. Higher process stability also leads to lower inputs of alkalizing compounds into digesters, which may directly affect the economic impact of the process [18].

Considering the suitability of two-phase AD for the treatment of vinasse, investigations are required to achieve a better understanding of the energetic potential of the H_2- and methane (CH_4)-rich biogas streams, i.e., biogas-H_2 and biogas-CH_4, respectively, resulting from vinasse biodigestion by providing the conditions for simulating scenarios in large-scale plants. The production of electricity is one of the potential uses of biogas that can maximize energy recovery [19] based mainly on the availability of consolidated efficient conversion technologies, such as engines and turbines [20]. Particularly in AD systems with phase separation, the biogas-H_2 resulting from the acidogenic step could play a key role in improving the generation of energy based on different technological approaches. Biogas-H_2 may be blended with the biogas collected from the methanogenic phase (biogas-CH_4) to form biohythane, which can improve the methane fuel properties, such as flame speed, range of flammability, and quenching distance [21]. A few recent studies have addressed the production of biohythane for bioenergy recovery from AD [22,23]. However, the energetic potential of biohythane is not addressed in detail in such cases. Another option includes the injection of biogas-H_2 into the methanogenic reactor, which represents an in situ biogas-CH_4 upgrade by increasing the CH_4 content via the conversion of H_2 and carbon dioxide (CO_2) by hydrogenotrophic methanogenesis [24,25].

In this context, this paper aims to assess different technological routes for bioenergy recovery from vinasse two-phase AD in first-generation sugarcane biorefineries based on the use of biogas-H_2 for different purposes: blending with biogas-CH_4 for biohythane production, injecting into methanogenic digesters for upgraded biogas-CH_4 production, and selling as a value-added product. Scenarios with two-phase AD without biogas-H_2 recovery and single-phase AD were also considered to assess the energy generation capacity of different prime movers, i.e., internal combustion engines (ICEs), gas turbines (GTBs) and GTBs followed by steam turbines (STBs). The influence of different alkalizing strategies in the methanogenic phase over the economic and environmental performance of the biorefinery was also assessed based on different approaches, such as the use of sodium bicarbonate ($NaHCO_3$) and sodium hydroxide ($NaOH$). The integration of vinasse biodigestion was compared with the usual scheme of sugarcane biorefineries in Brazil, in which vinasse is directed to fertirrigation without any processing. Experimental data from the literature [15,17,26] were used to simulate the performance of single- and two-phase AD systems, and the Virtual Sugarcane Biorefinery (VSB) methodological framework was used to compare the scenarios in terms of their techno-economic and environmental performance. The VSB is a tool developed by the Brazilian Bioethanol Science and Technology Laboratory (CTBE) used to assess the technical, economic, environmental and social impacts by integrating the entire sugarcane production chain [27]. In particular, this is the first study presenting a holistic technological assessment for recovering and using H_2 in full-scale sugarcane vinasse-fed biodigestion systems, in order to investigate the competitiveness of applying phase separation compared to conventional single-phase AD layouts.

2. Methods

2.1. Scenario description and inputs for the technological assessment

The reference scenario (CB-0) considered an annexed optimized biorefinery producing sugar, first-generation ethanol and electricity from conventional sugarcane during the harvesting season. This scenario also considered the use of energy cane during the inter-harvesting period of the conventional sugarcane. The recovery of lignocellulosic material from sugarcane fields (trash) was set to 50% and 100% (the leaves and tops of energy cane are harvested together with the stalks) for the harvesting and inter-harvesting periods, respectively [28]. Table 1 presents the input parameters and production data for the optimized biorefinery, which constitutes an improved standard plant characterized by a more efficient use of steam and, consequently, lower energy consumption levels [29]. Sugar (50% of the juice), ethanol (50% of the juice + molasses) and electric energy (100% of the bagasse + 50% of the straw) are the products obtained during the harvest season. Because the higher content of reducing sugars in energy cane hinders the crystallization of sucrose, only ethanol (100% of the juice) and electric energy (from energy cane lignocellulosic material) are obtained during the inter-harvest period (Table 1).

Performance data from both single- and two-phase AD

Table 1
Input data for the sugarcane biorefinery (sugar and ethanol production) and biodigestion plants.

Optimized annexed biorefinery			
Input data		Harvest	Inter-harvest
Feedstock		Conventional cane	Energy cane
Products		Ethanol, sugar and electricity	Ethanol and electricity
Period (days)		200	130
Milling capacity (TC[a])		4×10^6	1.7×10^6
Sugar production (ton)		205.5×10^3	–
Ethanol production (m^3)		214.5×10^3	95.2×10^3
Vinasse generation (m^3)		1837.5×10^3	824.3×10^3
Specific vinasse generation (m^3 per m^3 of ethanol)		8.6	8.6
COD-vinasse (g L^{-1})		28.3[b]	21.0[c]
Carbohydrates-vinasse (g L^{-1})		5.6[b]	5.6[b]
Thermophilic AD system			
Single-phase[d]		OLR = 25 kg-COD m^{-3} day^{-1}	
		ER-COD = 60.7%	
		MY = 0.234 Nm^3-CH$_4$ kg^{-1}COD-removed	
		Biogas-CH$_4$ composition: CH$_4$ (58.4%) + CO$_2$ (40.6%) + H$_2$S (1.0%)	
Two-phase	Acidogenic step[b]	OLR = 84.2 kg-COD m^{-3} day^{-1}	
		ER-COD = 21.2%	
		EC-carbohydrates = 70.5%	
		HY = 3.4 mol-H$_2$ mol^{-1}carbohydrates-converted	
		Biogas-H$_2$ composition: H$_2$ (37.0%) + CO$_2$ (63.0%)	
	Methanogenic step[e]	OLR = 25 kg-COD m^{-3} day^{-1}	
		ER-COD = 73.9%	
		MY = 0.301 Nm^3-CH$_4$ kg^{-1}COD-removed	
		Biogas-CH$_4$ composition: CH$_4$ (70.0%) + CO$_2$ (29.0%) + H$_2$S (1.0%)	

Notes: [a]TC = tonnes of cane; [b]Fuess et al. [15]; [c]Moraes et al. [10]; [d]Ferraz Jr. et al. [17]; [e]Fuess et al. [26].
Parameters (AD systems): OLR = organic loading rate; ER-COD = COD removal; MY = methane yield; EC-carbohydrates = carbohydrate conversion; HY = hydrogen yield.

processes used to simulate biogas generation are also detailed in Table 1 based on experimental data for thermophilic temperature conditions (55 °C) [15,17,26]. Although using experimental data to simulate full-scale processes may limit the extent of the analysis, the lack of pilot-to full-scale experiences with sugarcane vinasse in the Brazilian sucro-alcohol sector [26] dramatically reduces the availability of usable data in scenario prediction. Nevertheless, thermophilic systems constitute attractive alternatives for AD plants in distilleries and associate high treatment performance with the elimination of cooling systems prior to the digesters. Because vinasse is collected from distillation columns at temperatures above 85 °C, wastewater streams may reach the required temperature naturally in intermediate storage tanks and/or during the transportation to AD plants [10]. Five energy scenarios (CE-1 to CE-5) including AD were compared based on the different layouts for the generation of electric and thermal energy from biogas-H$_2$ and biogas-CH$_4$ streams. Table 2 and Fig. 1 present an overview of each proposed energy scenario based on a comparison between single- and two-phase AD systems and an assessment of different applications for biogas-H$_2$. Two-phase AD systems included approaches without biogas-H$_2$ production (CE-1), biogas-H$_2$ purification for sale (CE-2), biohythane production from biogas-H$_2$ and biogas-CH$_4$ blending (CE-3), and biogas-CH$_4$ upgrading by injecting purified biogas-H$_2$ into the methanogenic phase (CE-4). Single-phase AD was assessed in scenario CE-5. All scenarios considered the land application (fertirrigation) of the biodigested vinasse because AD reduces the organic pollution load without impairing the fertilizing potential of the vinasse.

2.2. Technical assessment: bioenergy generation from biogas

Bioenergy generation from biogas in each scenario was assessed via the simulation of three prime movers available in commercial scale for biogas-based power plants: ICE, GTB, and a combined cycle (CC), i.e., GTB + STB. The technical specifications for each prime mover are presented in Table 3. The simulations were developed

Table 2
Overview of the assessed scenarios considering the implementation of biodigestion plants for the treatment of vinasse in first-generation sugarcane biorefineries.

Scenario			CB-0	CE-1	CE-2	CE-3	CE-4	CE-5
AD plant			No	Yes	Yes	Yes	Yes	Yes
Phase separation			–	Yes	Yes	Yes	Yes	No
Acidogenic phase	pH control[a]		–	No	Yes	Yes	Yes	–
	Biogas-H$_2$ production		–	No	Yes	Yes	Yes	–
	Biogas-H$_2$	CO$_2$ removal[b]	–	–	Yes	No	Yes	–
		Use	–	–	Purification for sale	Blending with biogas-CH$_4^c$	Purification for injection into methanogenic reactor	–
Methanogenic phase	pH control[d]		–	Yes	Yes	Yes	Yes	Yes
	Biogas-CH$_4$ production		–	Yes	Yes	Yes	Yes	Yes
	Biogas-CH$_4$	CO$_2$ removal	–	No	No	No	No	No
		H$_2$S removal[e]	–	Yes	Yes	Yes	Yes	Yes
Biofuel for energy generation			–	biogas-CH$_4$	biogas-CH$_4$	biohythane	biogas-CH$_4$	biogas-CH$_4$

Notes: [a]Addition of NaOH to increase the pH of vinasse up to 6.5 [15]; [b]Considering the application of water scrubbing [30]; [c]Production of biohythane; [d]Addition of NaHCO$_3$ or NaOH, depending of the alkalizing strategy; [e]Considering the application of microaerobic conditions [30].
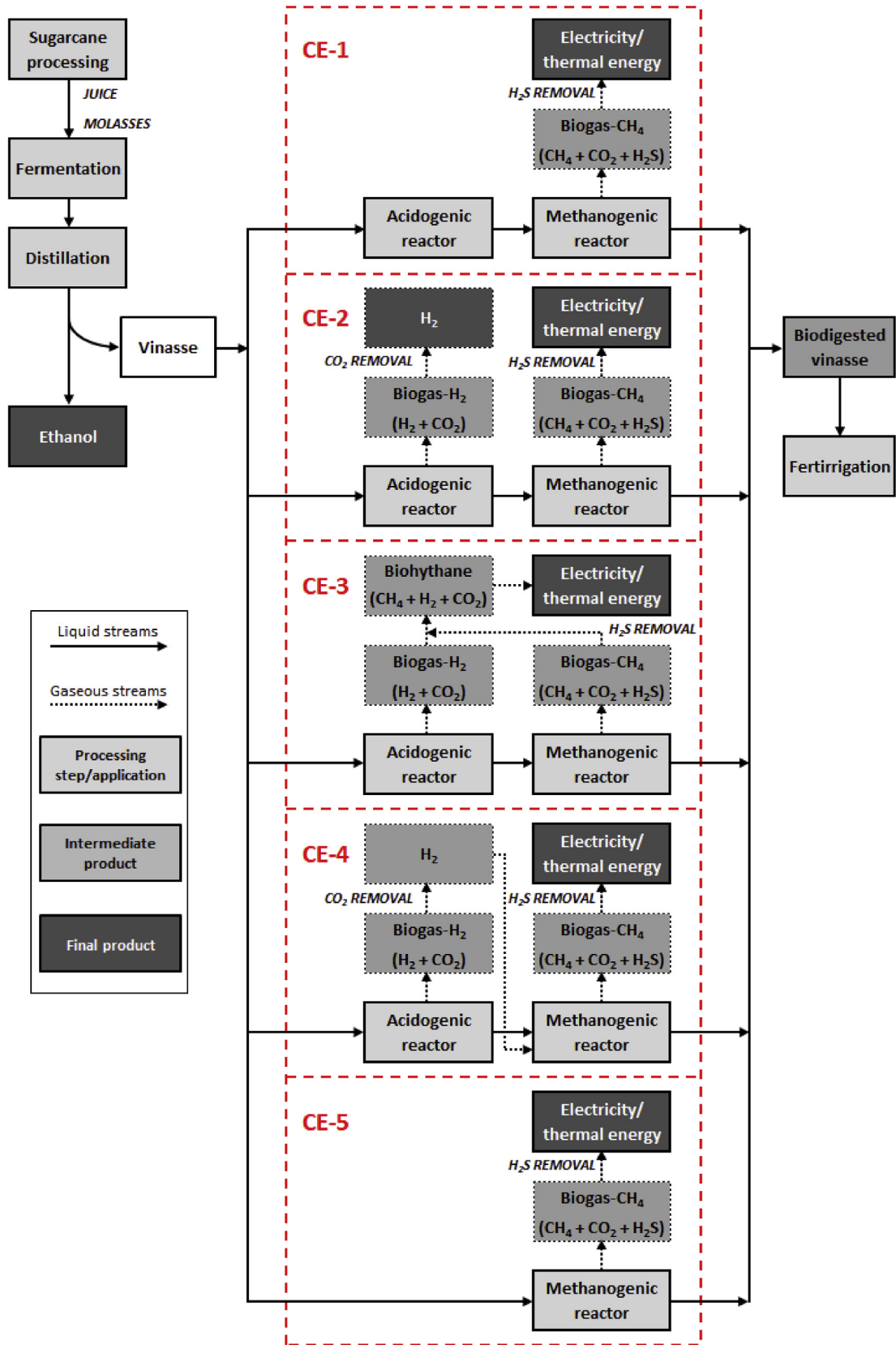
Fig. 1. Energy scenarios assessed for bioenergy recovery from sugarcane vinasse: CE-1 – two-phase AD without biogas-H_2 recovery; CE-2 – two-phase AD with biogas-H_2 purification for sale; CE-3 – two-phase AD with biohythane production from biogas-H_2 and biogas-CH_4 blending; CE-4 – two-phase AD with biogas-CH_4 upgrading by injecting purified biogas-H_2 into the methanogenic phase; and, CE-5 single-phase AD.

with the aid of the software Aspen Plus™ (Aspen Technology, Inc., Bedford, MA, USA) using the VSB framework based on the technical specifications from each prime mover. Electric and thermal energy generation was considered in scenarios with ICE and GTB, whereas only electric energy generation was simulated for the cases with CC. The recovery of thermal energy was based on the production of hot water (95 °C) from the dissipated heat in intercoolers, lube oil and jacket water (ICE) and exhaust gas (ICE and GTB). Hydrogen sulfide (H_2S) removal from biogas-CH_4 was considered in all cases using the maximum acceptable H_2S concentration for the ICE as a reference (~1000 ppmv, Table 3).

2.2.1. Basic calculations: biogas production and bioenergy recovery

The calculation of biogas-H_2 ($Q_{biogas-H2}$; m^3 h^{-1}) and biogas-CH_4 ($Q_{biogas-CH4}$; m^3 h^{-1}) flow rates was implemented in Aspen Plus™ according to Equations (1) to (3), in which the terms VFR, CH, EC_{CH}, HY, R, T, M, fH_2, COD_{acid}, ER_{COD}, MY, fCH_4 and COD_{raw} are the vinasse flow rate (m^3 h^{-1}), the concentration of carbohydrates in raw vinasse (g L^{-1}), the carbohydrate conversion efficiency in acidogenesis (dimensionless), the hydrogen yield (mol H_2 mol^{-1}CH), the ideal gas constant (0.082 atm L mol^{-1} K^{-1}), the operating temperature (55 °C), the molar mass of sucrose (0.342 kg mol^{-1}), the proportion of H_2 in biogas-H_2 (dimensionless), the COD of the acidified vinasse (g L^{-1}), the COD removal efficiency in methanogenesis (dimensionless), the methane yield (L CH_4 g^{-1}COD, 55 °C), the proportion of CH_4 in biogas-CH_4 (dimensionless) and the COD of the raw vinasse (g L^{-1}), respectively. Equation (2) was used to obtain $Q_{biogas-CH4}$ in scenarios CE-1 to CE-4, whilst Equation (3) was used in scenario CE-5. CH, COD_{raw}, EC_{CH}, HY, fH_2, ER_{COD}, MY and fCH_4 values are summarized in Table 1, based on experimental data presented elsewhere [15,17,26].

$$Q_{biogas-H2} = \frac{VFR \times CH \times EC_{CH} \times HY \times R \times (273.15 + T)}{1000 \times M \times fH_2} \quad (1)$$

$$Q_{biogas-CH4} = \frac{VFR \times COD_{acid} \times ER_{COD} \times MY}{fCH_4} \quad (2)$$

$$Q_{biogas-CH4} = \frac{VFR \times COD_{raw} \times ER_{COD} \times MY}{fCH_4} \quad (3)$$

Electric (EEP, MW) and thermal (TEP, MW) energy production values were obtained directly from the simulations of the ICE, GTB and CC, according to the technical specifications presented in Table 3 and biogas production resulting from the simulation of biodigestion systems (Equations 1–3). In turn, electric (η_{el}) and global (η_{global}) energy conversion efficiencies were calculated according to Equations (4) and (5), in which the terms EEP, BFR, LHV

and TEP are the electric energy production (kW), the biogas flow rate (m^3 h^{-1}), the lower heating value of biogas (MJ m^{-3}) and the thermal energy production (kW), respectively. BFR corresponds to the flow rate of biogas-CH_4 in scenarios CE-1, CE-2, CE-4 and CE-5 and to the flow rate of biohythane, i.e., biogas-H_2 + biogas-CH_4, in CE-3. LHV values were also directly obtained in simulations according to the content of CH_4 (biogas-CH_4) and H_2 + CH_4 (biohythane) in biogas streams.

$$\eta_{el} = \frac{EEP}{BFR \times LHV \times 3.6} \quad (4)$$

$$\eta_{global} = \frac{EEP + TEP}{BFR \times LHV \times 3.6} \quad (5)$$

2.3. Economic assessment methodology

The economic impact of implementing AD treatment plants in distilleries was assessed by calculating the internal rate of return (IRR), net present value (NPV), and discounted payback period of the project with a minimum acceptable rate of return (MARR) of 12% per year. The project lifetime, depreciation, and construction periods were set as 25, 10 and 2 years, respectively, and the tax rates were fixed at 34%. The investment and operating costs and selling prices were quoted in December 2015 using a conversion rate of USD 0.26 per unit of Brazilian real. The investment costs for the AD systems were estimated based on the design of treatment plants for both single- and two-phase processes as proposed by Fuess et al. [18], whereas reference data for the power plants (ICE, GTB, and CC) were obtained from the EPA [20]. Investments into CO_2 and H_2S removal systems were obtained from Muñoz et al. [30] considering water scrubbing (CE-2 and CE-4, biogas-H_2 purification) and the application of microaerobic conditions (CE-1 to CE-5, biogas-CH_4 purification), respectively.

With respect to the influence of the alkalizing strategy over the economics of the biorefinery, three alternatives were assessed based on the application of $NaHCO_3$ or NaOH into the methanogenic phase: [i] application of $NaHCO_3$ over the whole operating period of the plant ($NaHCO_3$-total), [ii] application of $NaHCO_3$ only during the startup phase of the reactors (50 first days, $NaHCO_3$-startup), and [iii] application of NaOH over the whole operating period (NaOH-total). For the alternatives "$NaHCO_3$-total" and "$NaHCO_3$-startup" dosages of 6.25 g $NaHCO_3$ $L^{-1}_{vinasse}$ [26] and 12.5 g $NaHCO_3$ $L^{-1}_{vinasse}$ [17] were considered for two- and single-phase systems, respectively, whereas for the alternative "NaOH-total," these values corresponded to 89.2 and 113.2 mg NaOH $L^{-1}_{vinasse}$, respectively, using the reference value of 4 g NaOH

Table 3
Technical specifications of the prime movers assessed for bioenergy recovery.

Prime mover	Technical specifications
ICE (J620 GS-F12,GE Jenbacher GmbH & Co. OHG, Jenbach, Austria)	Full load volumetric flow rate (air + biogas)[a] = 15,734 Nm³ h⁻¹ Compression ratio (ε) = 12.5 Thermal energy loss[a,b] = 1945 kW Maximum H_2S concentration = 2000 mg Nm⁻³CH_4 (~1000 ppm$_v$)
GTB[c] (KG2-3E, Dresser-Rand, Kirkegaardsveien, Norway)	Inlet pressure = 8 bar Exhaust gas temperature = 549 °C Maximum exhaust mass flow rate = 15 kg s⁻¹
STB (SST-110, Siemens AG − Energy Sector − Oil & Gas Division, Duisburg, Germany)	Inlet steam pressure = 131 bar Inlet steam temperature = 530 °C Outlet steam pressure = 0.6 bar

[a] Biogas flow rate = 1090 Nm³ h⁻¹; biogas lower heating value (LHV) = 23.4 MJ Nm⁻³.
[b] Excluding thermal energy recovery through hot water.
[c] Model simulated in scenarios considering the GTB as the sole prime mover and its coupling with the STB (combined cycle).
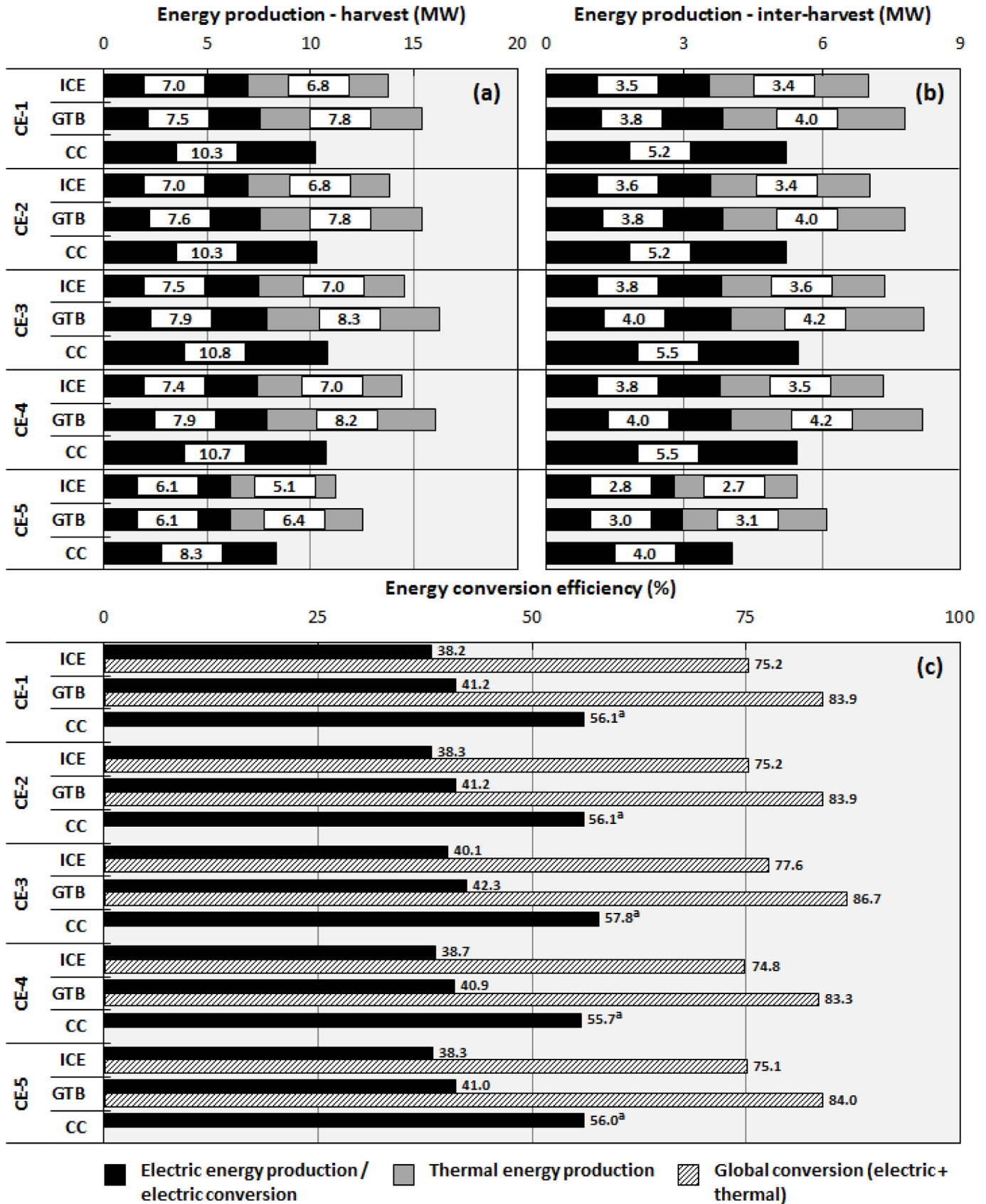
Fig. 2. Electric energy generation from biogas in the (a) harvesting and (b) inter-harvesting periods and (c) electric and total (electric + thermal) energy conversion for different prime movers.

kg^{-1}COD [8].

2.4. Environmental performance: life cycle assessment methodology

The environmental performance of each scenario was assessed and compared according to the life cycle assessment (LCA) methodology described in the ISO 14040 series of standards [31,32]. Worldwide, the LCA is the most frequently used methodology for the environmental assessment of products and processes, including systems targeting bioenergy production [2,29,33]. These assessments consider the impacts from resource use and emissions that are typically observed in the most common bioenergy systems. Substantially broader environmental aspects can be covered, ranging from greenhouse gas (GHG) emissions and fossil resource depletion to acidification, toxicity, and land use aspects.

SimaPro software [34] was used as a tool for this environmental assessment, and the ecoinvent database v2.2 [35] was used to obtain the environmental profile of the main inputs for the biorefinery, which considered both agricultural and industrial processes (e.g., diesel, fertilizers, pesticides and other chemicals used as inputs in the processes, such as the alkalizing compounds required for biodigestion). The use of resources and emissions to the soil, air, and water throughout the entire production chain were converted into different environmental impact categories using environmental impact assessment methods that are internationally recognized and published in the scientific literature. Selected impact categories from the ReCiPe Midpoint H method [36] were used to compare the environmental performance of ethanol in the assessed routes, including the global warming potential (GWP), which is measured in g–CO_2–eq kg^{-1} EtOH; human toxicity potential (HTP), which is measured in g-1,4-DB-eq kg^{-1} EtOH (where 1,4-DB corresponds to 1,4-dichlorobenzene); terrestrial acidification potential (TAP), which is measured in g–SO_2–eq kg^{-1} EtOH; freshwater eutrophication (FWE), which is measured in g-P-eq kg^{-1} EtOH; agricultural land occupation (ALO), which is measured in m^{2}a kg^{-1} EtOH; and fossil depletion potential (FDP), which is measured in g-oil-eq kg^{-1} EtOH.

The life cycle inventories used in this assessment were obtained from the results of agricultural (CanaSoft software, [37]) and industrial (technical assessment, section 2,2) simulations using the VSB framework. Because multiple products were obtained in each scenario, i.e., ethanol, sugar, electricity and H_2, depending on the biodigestion scheme, the environmental impacts were allocated to each product as predicted by the LCA methodology. In this study, the allocation procedure based on economic relationships was employed as described in the ISO 14040 and 14044 documents [31,32].

3. Results and discussion

3.1. Bioenergy generation from biogas

Data on the bioenergy generated from biogas are depicted in Fig. 2a–b and include both the electric and thermal fractions. An overall analysis indicates that the application of biohythane as fuel (CE-3) could lead to energy gains compared with the use of biogas-CH_4, regardless of the prime mover and the AD process scheme, i.e., single- or two-phase systems. Such a pattern results from a more efficient combustion of CH_4 based on the previously highlighted advantages, which increased the conversion of biogas into electric energy, regardless of the prime mover (Fig. 2c). Particularly for biogas streams, the addition of H_2 minimizes dilution effects from CO_2, which allows for the use of lean-burn (excess air supply) conditions in engines. In such cases, the provision of higher oxygen levels also leads to a more efficient combustion, which favors the

role of H_2 as an enhancer of energy generation [38].

Biogas-H_2 purification followed by H_2 injection into the methanogenic reactors (CE-4) leads to similar results compared with CE-3 (Fig. 2a–b). In this case, energy gains are related to an increase in the lower heating value (LHV) of biogas-CH_4, i.e., 21.96 MJ m^{-3} (CE-4) vs. 20.92 MJ m^{-3} (CE-1 and CE-2), based on a higher CH_4 content (~75%) in biogas. Such scenarios simulated the enhancement of hydrogenotrophic activity in the methanogenic phase; therefore, the reduction in CO_2 content in the biogas-CH_4 also improved its combustion properties. Compared with the use of biohythane (CE-3), the main drawback from scenario CE-4 is related to the need to remove CO_2 from biogas-H_2 prior to its injection into the methanogenic phase to prevent an imbalance of inorganic carbon levels in the reactor as well as energy losses because of the accumulation of CO_2 in biogas-CH_4. Although biohythane formation via biogas-H_2 and biogas-CH_4 blending decreased the LHV of biogas-CH_4, i.e., 16.07 MJ m^{-3} (CE-3) vs. 20.92 MJ m^{-3} (CE-1 and CE-2), the improved combustion properties of H_2 most likely offset such dilution effects in scenario CE-3.

An alternative method of utilizing biogas-H_2 could be the direct generation of electricity in fuel cells after the removal of CO_2. In this case, an increment of approximately 382 kW would be observed in the amount of electricity generated in the harvesting period in scenarios CE-1/CE-2, where the H_2 from the acidogenic phase was not recovered (CE-1) or used to directly recover bioenergy (CE-2). Estimates considered specifications from a Ballard ClearGen fuel cell with an electric conversion efficiency of 40%. However, comparatively higher electric increments were simulated through both the application of biogas-H_2 to biohythane production (CE-3; 502–545 kW, respectively, for ICE and CC) and the in loco biogas-CH_4 upgrade via enhanced hydrogenotrophic methanogenesis (CE-4; 467–479 kW, respectively, for ICE and CC), and these simulations also used scenarios CE-1/CE-2 as the baseline. In addition to the lower electricity generation, the investment costs with the fuel cells would be over 90–150% of the incremental investments required by the application of biohythane (CE-3) or upgraded biogas-CH_4 (CE-4) into ICEs, GTBs, or CCs, which features the use of conventional prime movers as a more attractive approach for exploiting both biogas-H_2 and biogas-CH_4 streams.

Bioenergy generation in scenarios with single-phase AD processes (CE-5) reached values that were at least 20% lower compared with two-phase schemes (Fig. 2a–b), regardless of the strategy used to implement the biogas-H_2 and the type of prime mover. Despite the slightly lower influent COD compared with single-phase reactors, such results reflect the enhanced performance of methanogenic reactors preceded by acidogenic systems as observed in the higher organic matter conversion rates and methane yields (Table 1). Fig. 3a–b compare the electric energy production levels observed herein with data from similar studies (based on single-phase processes), also indicating higher levels for systems with phase separation. In addition to the advantages of pre-acidifying the wastewaters, the observed differences also resulted from specific assumptions considered in each analysis, such as the size of the ethanol plant and mainly the specific vinasse generation. The vinasse generation observed in this study (8.6 m^3 per m^3 of ethanol, Table 1) was considerably lower than the average values observed in ethanol plants (12–14 m^3 per m^3 of ethanol – [4,9,39]). Nevertheless, the operation of AD-power plants during the inter-harvest could increase electric energy generation by 50% (Fig. 3b), which was based on values from the harvesting period as reference.

Considering a wider analysis, the electric energy obtained from vinasse AD (8.35–12.97 kWh per ton of sugarcane – TC) during the harvesting period (CE-1 to CE-4) could replace 40–60% of the biorefinery electricity consumption (21.1 kWh TC^{-1}, [40])

depending on the prime mover. With reference to the thermo-electric production from bagasse burning in cogeneration systems (46.2 kWh TC^{-1}, [40]), over 50% of the electric energy exported to the grid (25.1 kWh TC^{-1}, [40]) could be achieved in AD-power plants with CC. Regarding the heat recovery within the scenarios with ICE and GTB (8.17—9.94 kWh TC^{-1}), slightly more than 2—3% of the thermal energy consumed in distilleries (300 kWh TC^{-1}, [41]) could theoretically be replaced with biogas, which characterizes the maximization of electric energy production as a more attractive option for the sucro-energetic sector.

The electricity obtained from biogas in the simulated biorefinery could reach values in the range of 33.4—51.9 × 10^3 MWh (harvest) and 11.2—17.2 × 10^3 MWh (inter-harvest) depending on the type of prime mover. AD-power plants based on the application of bio-hythane to the CC could supply populations as high as 140 and 60 thousand inhabitants in the periods of harvest (51.9 × 10^3 MWh) and inter-harvest (17.2 × 10^3 MWh), respectively, considering a

monthly per capita energy consumption equivalent to 54.3 kWh $inhab^{-1}$ (monthly residential energy consumption of 163 kWh based on an average of three inhabitants per residence [42]). The total electric power achievable from vinasse AD for the 2014/2015 sugarcane harvest season considering the total amount of vinasse produced in this period in Brazil could vary within the range of 841—1319 MW based on a total ethanol production of 28.66 billion liters for the period [43] and the energy potential estimated for biogas within the scenarios with phase separation. In the context of Brazilian hydroelectric power generation, approximately 15—20% of the production from Tucuruí (8540 MW, [44]) and Itaipu (7000 MW, [44]) dams could be replaced by the energy from biogas, whereas more favorable patterns could be observed in relation to thermoelectric generation. Biogas energy obtained from vinasse could replace 35—55% of the total electricity produced by the 10 largest fuel oil-based Brazilian thermal plants in 2014 (2416 MW, [44]). For coal-based plants, such replacement values would vary
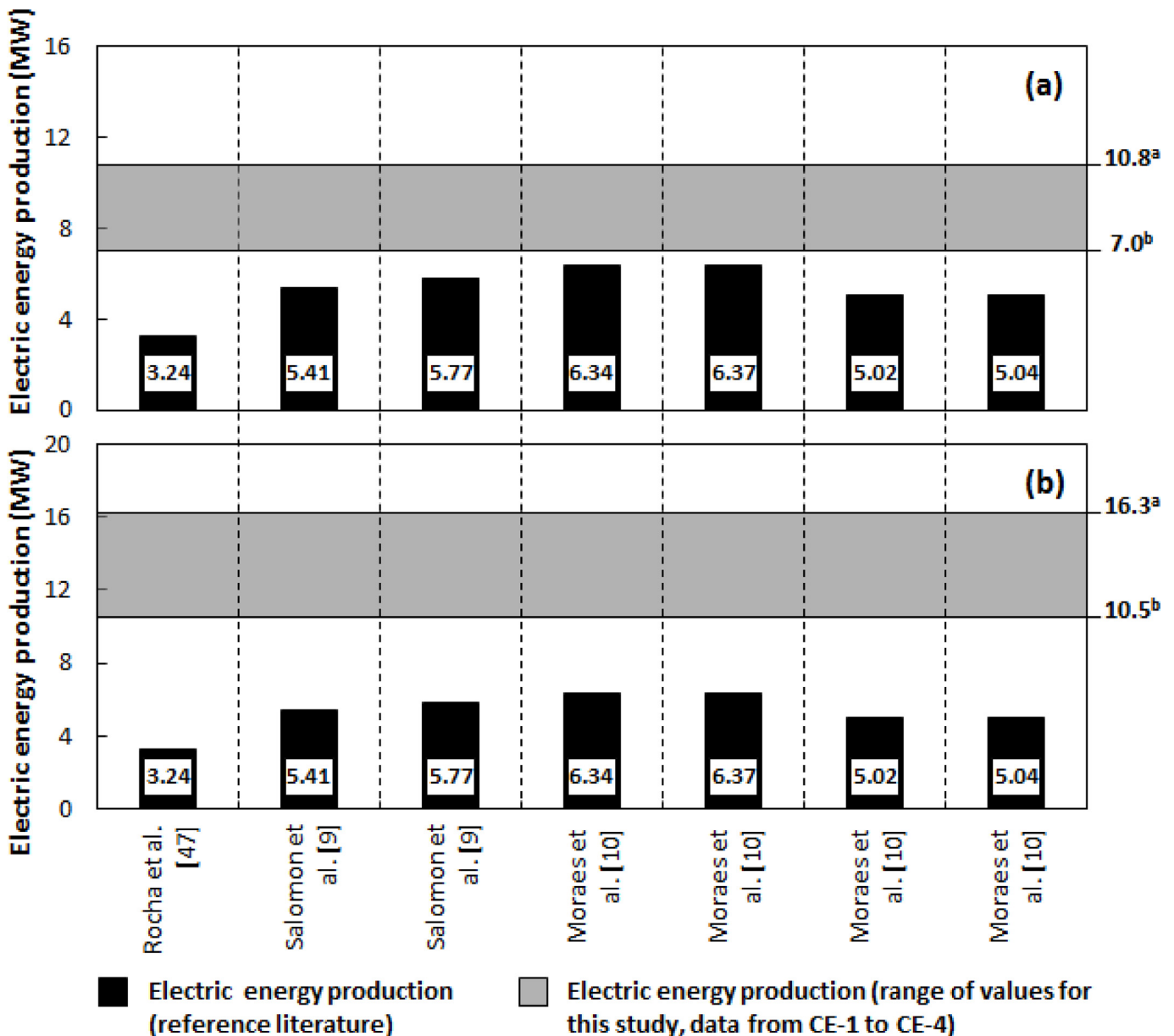

Fig. 3. Electric energy generation from sugarcane vinasse in various studies compared with the production levels observed in the (a) harvesting and (b) harvesting + inter-harvesting periods. Note: Electric energy generation is based on scenarios [a]CE-3-CC and [b]CE-1-ICE. Comparative data obtained from [9,10,47].

between 25 and 40% based on the accumulated electric production from the 10 largest Brazilian plants (3277 MW, [44]).

3.2. Economic assessment

Phase separation would lead to investment costs that are approximately 60% higher compared with single-phase AD schemes (10.16 vs. 6.24 million USD), and the main expenses are associated with the construction of reactors and equalization tanks. Fig. 4a details and compares the total investment costs for both AD and power plants in each scenario and shows that the values range from 22.12 to 26.91 million USD and from 16.58 to 17.79 million USD for two- and single-phase AD processes, respectively. Investments with the power plant accounted for more than 50% of the total installation costs (Fig. 4b) regardless of the prime mover, with higher values observed for scenarios with GTB as the sole prime mover because of the higher costs associated with heat recovery systems used for thermal energy generation. Biogas purification systems accounted for 7–8% of the total costs in the scenarios with CO_2 removal from biogas-H_2 (CE-2 and CE-4; Fig. 4b), whereas the investments associated with H_2S removal from biogas-CH_4 accounted for less than 1% of the total costs (CE-1 to CE-5; Fig. 4b). The installation costs with AD-power plants corresponded to less than 10% of the total investments estimated for the sugarcane biorefinery in CB-0 (280.67 million USD), regardless of the prime mover.

Despite the higher investment costs (Fig. 4a), the economic parameters indicated that the implementation of AD-power plants

in the reference biorefinery would lead to feasible scenarios based on the positive NPV (USD 208.58–219.86 million) and higher IRR values relative to the MARR (12%) (Fig. 5). For a given energetic scenario, changing the type of prime mover led to minimal alterations in the NPV, IRR, and payback period values, although the best conditions could always be associated with the use of a CC. Focusing on the cases with phase-separation AD plants, the most profitable option was achieved in scenario CE-1, which did not include the collection and use of biogas-H_2. Despite the lower energy production in CE-1 (Fig. 2), specific characteristics of the plant favored such scenario in economic aspects, with emphasis on lower investments regarding the power plant (Fig. 4a).

The comparison between single- and two-phase AD systems depends directly on the type of alkalizing strategy used in the methanogenic phase because of the influence of the type and quantity of chemicals, i.e., $NaHCO_3$ or $NaOH$, over the operational expenditure (OPEX) in the assessed scenarios. For the strategy "$NaHCO_3$-total", the NPV and IRR values would be 30% and 9% higher in the scenarios with phase separation, respectively (CE-1 to CE-4; Fig. 5). Slightly lower payback periods (6.6–6.8 vs. 7.6–7.7 years), which represent the time required to recover investment costs, also confirm that the best economic performance occurs with two-phase AD systems compared with single-phase processes. Despite the lower investment (24–27%; Fig. 4) and lower operating costs compared with scenarios CE-1 to CE-4, the higher costs of the chemicals ($NaHCO_3$) in scenarios with single-phase AD (CE-5) (28.53 vs. 15.05–16.70 million USD) would lead to a lower profitability, which is reflected in the higher production costs for ethanol
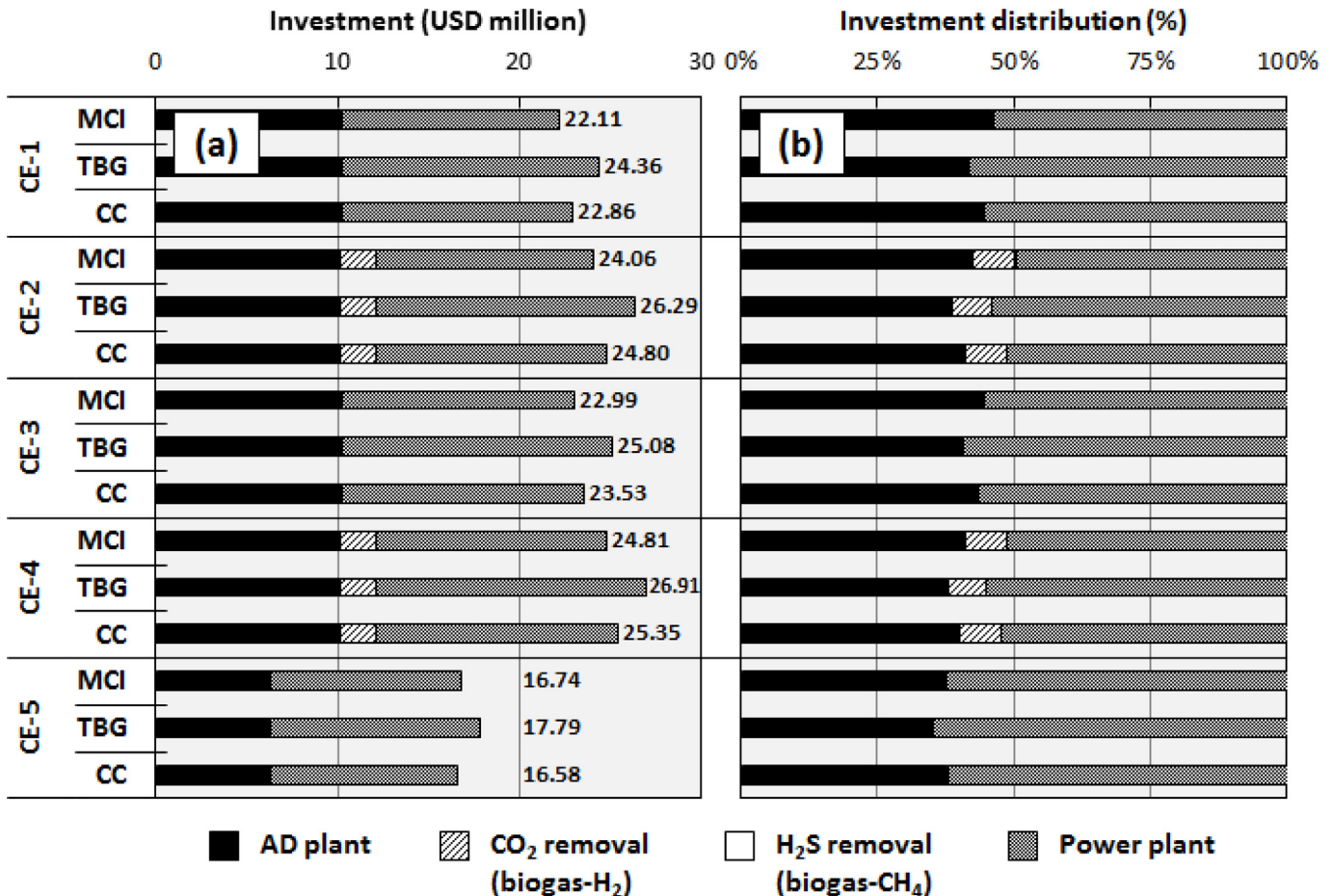

Fig. 4. (a) Total investment costs with AD-power plants and (b) the relative distribution of investment costs according to the plant components.

(USD 0.28 per liter) and electric energy (USD 27.9 per MWh) observed in CE-5. The production costs for both ethanol and electric energy varied within the ranges of USD 0.25−0.26 L^{-1} and USD 25.6−26.0 MWh^{-1}, respectively, in scenarios CE-1 to CE-4. Nevertheless, such an alkalizing strategy may not be feasible in large-scale AD plants because the annual revenues from the electric energy produced via biogas would be less than 20% of the costs associated with the chemicals used in plants with phase separation (2.60 vs. 16.70 million USD, CE-3-CC).

Distinct patterns were observed with the alternative alkalizing strategies proposed herein. The application of $NaHCO_3$ during only the startup period of the methanogenic phase considerably increased the NPV (259.95−271.23 million USD) and IRR (21.9−22.4%) and reduced the payback period (5.8−6.0 years) in all scenarios, regardless of phase separation. For this alkalizing strategy, single-phase AD would be less economically attractive only when compared with scenarios CE-1 and CE-2. By replacing $NaHCO_3$ with NaOH (NaOH-total), phase separation would not produce positive economic effects compared with single-phase processes, regardless of how the biogas-H_2 is used, despite the similar economic performance (NPV = 270.19−281.47 million USD, IRR = 22.2−22.7%, payback = 5.6−5.8 years for CE-1 to CE-4; NPV = 282.71−285.32 million USD, IRR = 22.9−23.0%, payback = 5.5 years for CE-5; Fig. 5a−f). The lower operating costs
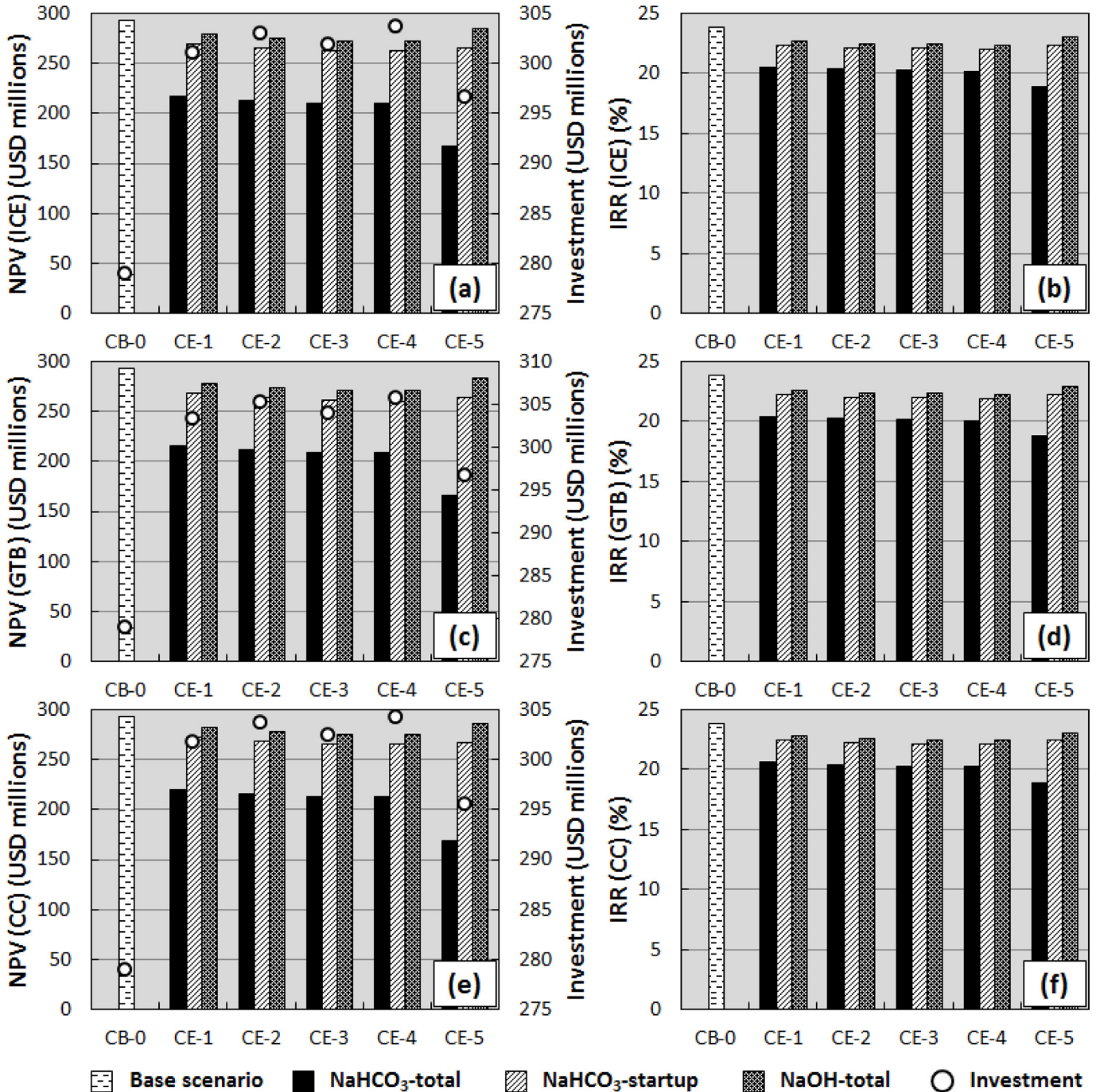

Fig. 5. Net present value (NPV), total investment and internal rate of return (IRR) for the scenarios with (a) and (b) an internal combustion engine (ICE), (c) and (d) a gas turbine (GTB), and (e) and (f) a combined cycle (CC).

with AD plants in scenario CE-5 explain the pattern in which the lower revenues from electric energy sales are offset.

Finally, although the base scenario (CB-0) indicated better economic results compared with the layouts implementing AD (NPV = 293.40 million USD and IRR = 23.9%; Fig. 5, and payback = 5.2 years), such a configuration may not be considered an adequate reference for comparison purposes. The reference scenario includes the direct land disposal of vinasse *in natura*, which may trigger a large variety of negative environmental effects

[4] and prevent bioenergy recovery through AD. In addition, the NPV and IRR values obtained for scenarios that implemented AD systems may be as high as the values observed for CB-0 depending on the alkalizing strategy, even when phase separation is considered, thereby coupling the positive technical and economic aspects of such systems. Further improvements in the economic performance of the AD-based scenarios could be achieved by including the production of an organomineral fertilizer from concentrated biodigested vinasse [45] because of the potential reductions in
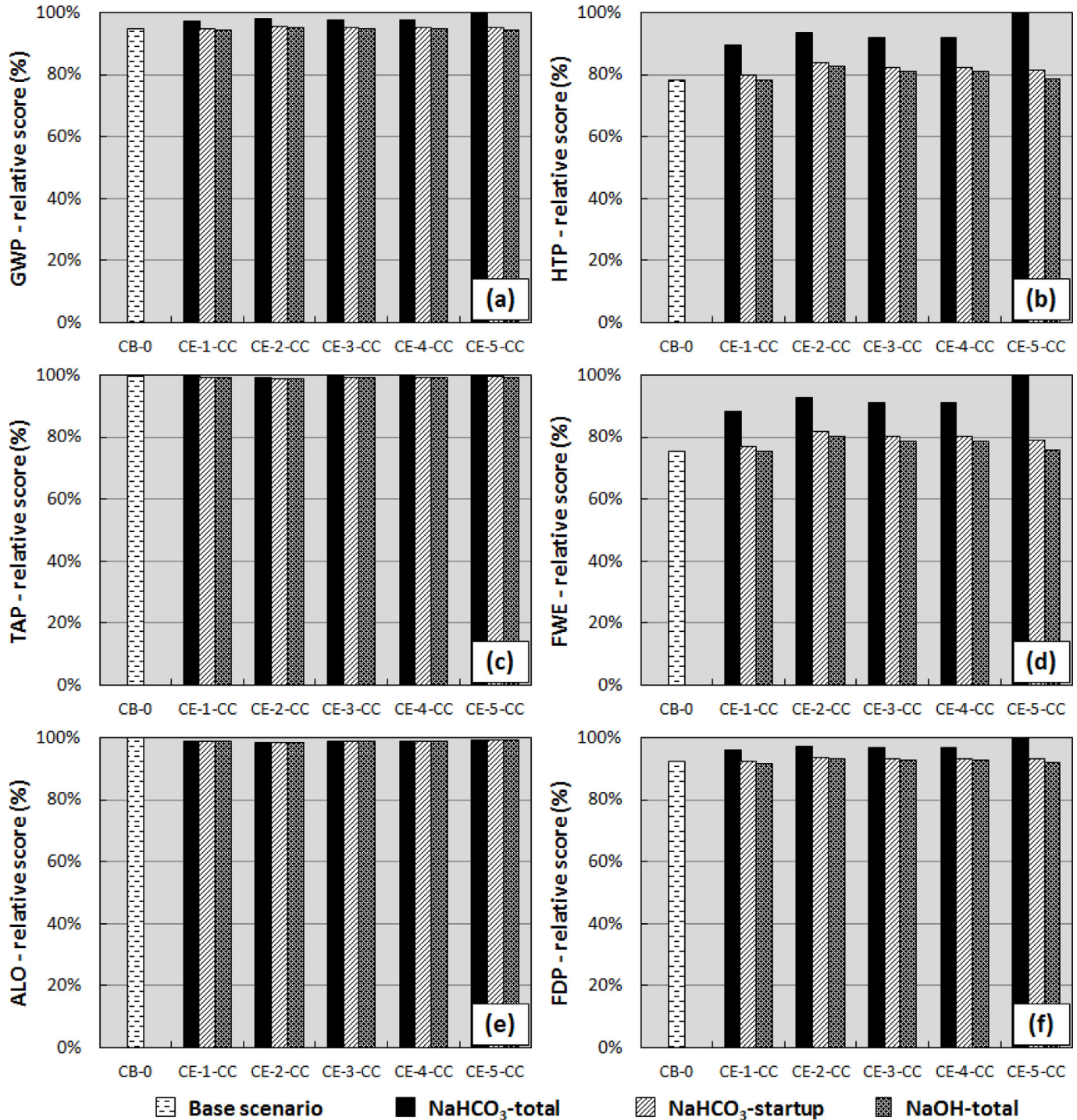

Fig. 6. Comparative environmental scores for ethanol according to the different impact categories: (a) global warming potential (GWP), (b) human toxicity potential (HTP), (c) terrestrial acidification potential (TAP), (d) freshwater eutrophication (FWE), (e) agricultural land occupation (ALO), and (f) fossil depletion potential (FDP).

fertilization costs for sugarcane production. The high liquid fraction of raw vinasse economically hinders its transportation for long distances, which limits its land disposal to a few kilometers from the biorefinery. In turn, the production of an organomineral fertilizer, which could include the concentration of the biodigested vinasse coupled to nitrogen supplementation [45], as well as the blending with other biorefinery byproducts (e.g. sugarcane trash and boiler ashes), would enable achieving higher distances, directly reducing inputs with mineral fertilization.

3.3. Environmental performance assessment

The LCA only considered scenarios based on the use of a CC for bioenergy generation because larger electric energy production levels could be coupled to minimal changes in the economic performance compared with use of the other prime movers as previously discussed (sections 3.1 and 3.2). The comparative environmental impacts of ethanol production for the selected impact categories in all scenarios are presented in Fig. 6, also considering different alkalizing strategies. The impacts for a given category are scored in each scenario and compared with each other, with the worst environmental performance associated with a value of 100%. An overall analysis of the relative environmental impacts indicates similar performance for the categories GWP (Fig. 6a), TAP (Fig. 6c), and ALO (Fig. 6e), regardless of whether vinasse biodigestion and phase separation were implemented. Discrepancies related to the alkalizing strategy were also minimal in such cases. A similar pattern was also observed for the categories HTP (Fig. 6b), FWE (Fig. 6d), and FDP (Fig. 6f) when considering the alkalizing strategies NaHCO₃-startup and NaOH-total, whereas the worst environmental performance was clearly related to the strategy NaHCO₃-total, primarily for single-phase AD schemes. Such results are similar to the trends observed for the economic assessment

because the main drawbacks were associated with the high inputs of NaHCO₃. The use of NaOH to adjust the pH of the raw vinasse prior to the acidogenic phase increased the environmental impacts of scenarios CE-2 to CE-4 only slightly compared with that of CE-1 based on the relative scores for the categories HTP (Fig. 6b), FWE (Fig. 6d), and FDP (Fig. 6f).

The environmental impact of ethanol production classified according to the categories GWP, HTP, FWE, and FDP is presented in Fig. 7 to highlight the effects of applying high dosages of NaHCO₃. The drawbacks resulting from NaHCO₃ production (Solvay process) are primarily based on the use of fossil fuels for thermal energy production, and they considerably increased the scores for GWP (Fig. 7a) and FDP (Fig. 7d). The high scores related to the biodigestion inputs in the category HTP (Fig. 7b) were also related to the consumption of fossil fuel for NaHCO₃ production because the burning process increases the emissions of toxic compounds. The use of ammonia in the Solvay process also impacts the category HTP, although it generates lower scores compared with the emissions from fossil fuel burning. However, the emissions from nitrogen compounds, primarily from the use of ammonia, are the main factors that contributed to the high scores associated with NaHCO₃ in the category FWE (Fig. 7c), although bicarbonate itself may stimulate the proliferation of aquatic macrophytes [46]. Junqueira et al. [45] also associated certain environmental drawbacks with the use of NaHCO₃ in the biodigestion plants of sugarcane-based biorefineries treating vinasse; however, the impacts were a result of the indirect use of NaOH in the AD system because of its reaction with CO_2 for the *in loco* production of NaHCO₃.

Despite the drawbacks, particularly those associated with the use of NaHCO₃ in the AD plant, the environmental performance of ethanol production was severely impacted in the HTP and FWE categories only when the NaHCO₃-total strategy was implemented (Fig. 7). An overall analysis indicated that the impact from
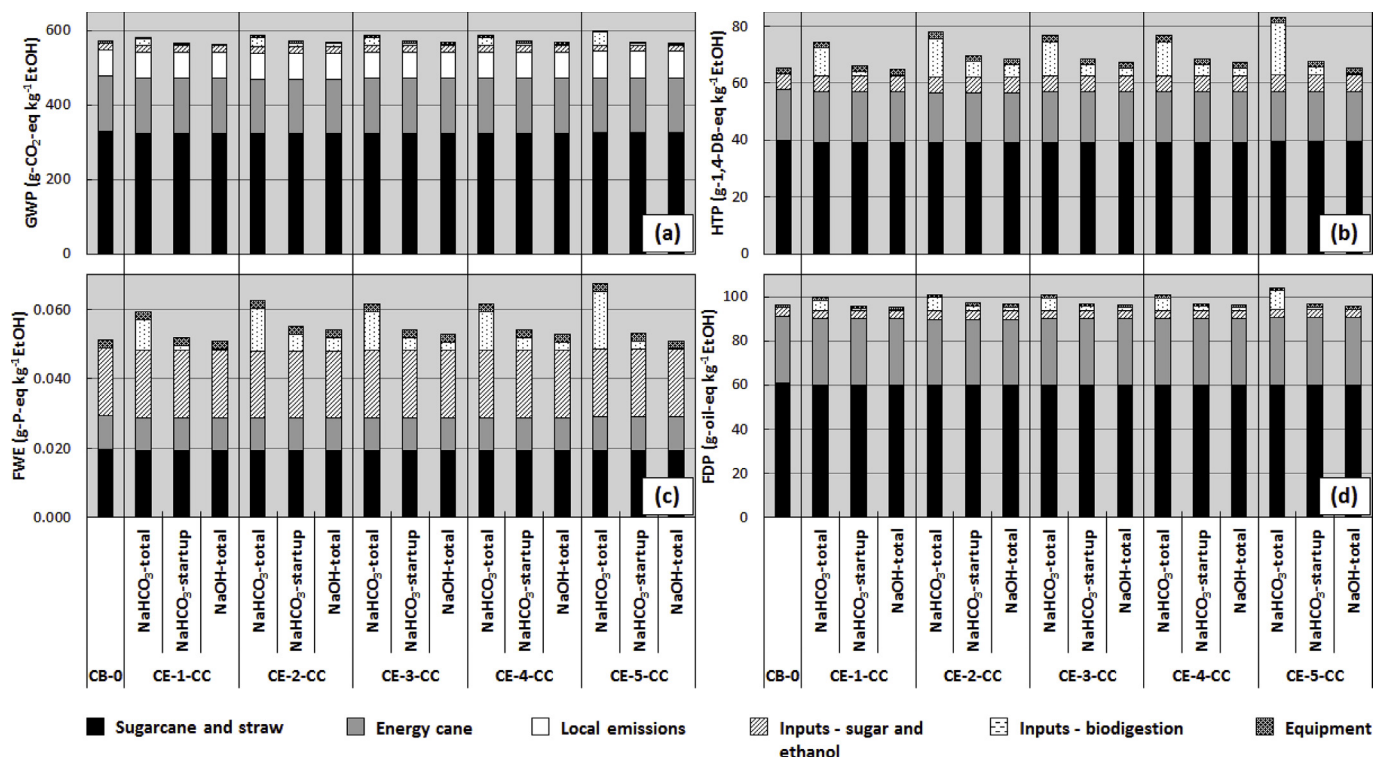

Fig. 7. Breakdown of the environmental impact on selected categories for ethanol production in different scenarios: (a) global warming potential (GWP), (b) human toxicity potential (HTP), (c) freshwater eutrophication (FWE), and (d) fossil depletion potential (FDP).

implementing AD systems in biorefineries was considerably lower compared with the impact observed in the agricultural phase (Fig. 7). Furthermore, optimizing the alkalizing strategy (which is represented by the use of low dosages of NaOH in this study) slightly minimized the environmental impact from ethanol production. Such results indicate the possibility of associating energetic and environmental (to a less extent) gains with the maintenance of a comparable economic performance as the base scenario, i.e., without biodigestion, even when considering phase separation for the AD scheme.

4. Conclusions

The following conclusions can be drawn from this study:

- Biodigestion of vinasse with phase separation greatly enhances electric energy generation (20–30% compared to single-phase schemes) without impairing the profitability of the sugarcane biorefinery, depending on the alkalinization strategy;
- Optimizing the alkalinization of methanogenic systems characterizes a determining factor to improve both the economic and environmental performance of AD plants by reducing operating costs and the risks associated to human toxicity and fresh water eutrophication;
- Enhanced electric energy generation may represent a more attractive option for distilleries compared with thermal energy because over 50% of the electric energy exported to the grid could be achieved in AD-power plants with a combined cycle; and,
- Implementing full-scale AD plants to treat sugarcane vinasse should be facilitated by using mechanisms that stimulate more efficient systems with regard to electric energy production and polluting load reductions, such as subsides to reduce investment costs and increase revenues via bioenergy.

Acknowledgments

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