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*Supplementary Materials*

# Exploring Potentials for Bioresource and Bioenergy Recovery from Vinasse, the "New" Protagonist in Brazilian Sugarcane Biorefineries

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**Table S1.** Compositional characterization of sugarcane vinasses from juice and blends of juice and molasses. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| Parameter | | Siqueira et al. [60] | Santos et al. [220] | Santos et al. 221] | Santos et al. [222] | Ferraz Jr. et al. [211] | Reis et al. [219] | Fuess et al. [44] | Fuess et al. [88] | Fuess et al. [77] | Moraes et al. [82] | Santos et al. [78] | Santos et al. [78] | Piffer et al. [79] | Sánchez et al. [43] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Organic fraction | COD[a] | 36.0-49.0 | 30.4-33.8 | - | 30.4-33.0 | 35.2 | 42.8 | 28.3 | 22.9-35.8 | 19.5-49.0 | - | 42.9 | 17.8 | 18.9-28.1 | 48.2 |
| | BOD[a] | - | - | - | - | 16.7 | - | 14.6 | 14.4-21.9 | 8.8-23.2 | - | 23.2 | 8.8 | 8.6-14.9 | 23.2 |
| | BOD/COD | - | - | - | - | 0.47 | - | 0.51 | 0.40-0.68 | 0.39-0.48 | - | 0.54 | 0.49 | 0.41-0.67 | 0.48 |
| | TCarb[a] | - | - | 10.6-16.3 | - | 4.1 | - | 5.6 | - | 3.9-7.3 | - | 4.7 | 4.3 | 2.3-4.5 | 5.2 |
| | TVA[b] | 4,436-5,882 | - | - | - | - | 3,012 | - | - | - | - | - | - | - | - |
| | HFo[b] | - | 978-3,556 | - | - | - | - | - | - | - | - | - | - | - | - |
| | HAc[b] | - | 348-1,617 | 2,248-4,917 | 526-1,617 | - | - | - | - | 153-1,722 | 220 | 1,117 | 153 | 141-1,392 | 330 |
| | HLa[b] | - | 4,558-12,697 | 3,421-5,248 | 5,960-7,889 | - | - | - | - | 1,050-2,550 | 10,130 | 1,735 | 917 | 305-967 | 1,700 |
| | HPr[b] | - | 314-911 | 1,644-4,680 | 582-874 | - | - | - | - | 0-127 | - | 64 | - | 0-646 | - |
| | HBu[b] | - | 269-885 | 1,396-4,219 | 497-613 | - | - | - | - | 0-468 | 610 | 468 | - | 0-463 | - |
| | HIBu[b] | - | 1,547-4,597 | - | 2,367-4,597 | - | - | - | - | - | 3,410 | - | - | - | - |
| | HMa[b] | - | 2,639-6,168 | - | - | - | - | - | - | - | 10,460 | - | - | - | - |
| | HSu[b] | - | 967-3,624 | 1,364-3,523 | - | - | - | - | - | - | 3,720 | - | - | - | - |

**Table S1.** Compositional characterization of sugarcane vinasses from juice and blends of juice and molasses. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| **Parameter** | | **Siqueira et al. [60]** | **Santos et al. [220]** | **Santos et al. 221]** | **Santos et al. [222]** | **Ferraz Jr. et al. [211]** | **Reis et al. [219]** | **Fuess et al. [44]** | **Fuess et al. [88]** | **Fuess et al. [77]** | **Moraes et al. [82]** | **Santos et al. [78]** | **Santos et al. [78]** | **Piffer et al. [79]** | **Sánchez et al. [43]** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nutrient content | TKN[b] | 570-1,603 | 436-861 | 1,354-1,619 | 700-1,200 | 700 | 244 | 862 | 629-1,404 | - | 840 | - | - | 252-651 | 590 |
| | P[b] | 35-111 | 147-181 | 208-236 | 180-240 | 160 | 3,796 | 113 | 26-154 | - | - | - | - | 25-45 | 40 |
| | K[b] | 2,334-3,147 | - | 4,200-4,800 | 3,800-4,500 | - | 4,500 | - | 1,330-4,010 | - | 2,650 | - | - | 1,650-3,290 | - |
| | Ca[b] | 741-1,502 | - | 532-659 | 698-757 | - | 757 | - | 458-2,240 | - | 510 | - | - | 350-580 | - |
| | Mg[b] | 354-543 | - | 415-448 | 367-580 | - | 580 | - | 145-189 | - | 260 | - | - | 221-322 | - |
| | $SO_4^{2-}$[b] | 2,300-2,900 | 1,400-2,600 | 2,100-2,900 | 1,800-2,600 | 1400 | 1,400 | 1,7 | 2,300-3,701 | 1,042-2,500 | 900 | 2,000 | 1,225 | 981-1,592 | 2,050 |

Notes: [a]Values in g $L^{-1}$; [b]Values in mg $L^{-1}$. Nomenclature: COD = chemical oxygen demand; BOD = biochemical oxygen demand; TCarb = total carbohydrates; TVA = total volatile acids; HFo = formic acid; HAc = acetic acid; HLa = lactic acid; HPr = propionic acid; HBu = butyric acid; HIBu = iso-butyric acid; HMa = malic acid; HSu = succinic acid; TKN = total Kjeldahl nitrogen; P = phosphorus; K = potassium; Ca= calcium; Mg = magnesium; $SO_4^{2-}$ = sulfate.

**Table S2.** Alternative (bio)technological applications proposed for sugarcane vinasse. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| (Bio)technol. approach | Reference | Objective and motivation of the study |
|---|---|---|
| Biomass/feed production | Costa et al. [174] | *Objective:* assess different approaches for the management of biodigested sugarcane vinasse: post-treatment for reducing the polluting load, fertirrigation, and fish food production<br>*Motivation:* define an alternative approach to reduce the residual polluting load of biodigested sugarcane vinasse |
| | Ricci et al. [108] | *Objective:* production of single-cell protein (SCP)[a] by growing *Candida utilis* var. major NRR-T-1084 on raw sugarcane vinasse<br>*Motivation:* enhance the economic feasibility of SCP production by reducing costs with the substrate |
| | Kadioğlu and Algur [102] | *Objective:* growth of microalgae (*Chlamydomonas reinhardii*) on raw sugarcane vinasse<br>*Motivation:* reduction of the polluting load of vinasse (elimination of residual inorganic nutrients) coupled to the production of SCP |
| | Nitayavardhana and Khanal [56] | *Objective:* production of protein-rich fungal biomass (*Rhizopus microsporus* var. *oligosporus*) on vinasse as substrate<br>*Motivation:* reduction of the polluting load of vinasse coupled to the production of high-value animal feed |
| | Bonini [76] | *Objective:* assess the heterotrophic cultivation of microalgae (*Aphanothece microscopica Nägeli* and *Chlorella vulgaris*) on different substrates (glucose, glycerol, acetate, and raw sugarcane vinasse)<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse (reduction of the organic and inorganic polluting loads)/ production of SCP |
| | Marques et al. [103] | *Objective:* growth of microalgae (*Chlorella vulgaris*) on raw and biodigested sugarcane vinasse<br>*Motivation:* use of residues for reducing costs with the implementation of full-scale microalgae-based biodiesel plants |
| | Ramirez et al. [57] | *Objective:* growth of microalgae (*Scenedesmus* sp.) on raw sugarcane vinasse<br>*Motivation:* reducing costs of products (e.g. biofuels and pigments) derived from microalgae by recycling nutrients from residues |
| | Pires et al. [107] | *Objective:* production of microbial biomass (SCP) by *Saccharomyces cerevisiae* CCMA 0137, *S. cerevisiae* CCMA 0188, and *Bacillus subutilis* CCMA 0087, coupled to the reduction of the polluting load of vinasse<br>*Motivation:* reduction of the volume of vinasse directed to fertirrigation/ value adding to vinasse |

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| **(Bio)technol. approach** | **Reference** | **Objective and motivation of the study** |
|---|---|---|
| Biomass/feed production | Santos et al. [104] | *Objective:* growth of microalgae (*Spirulina maxima*) on raw sugarcane vinasse<br>*Motivation:* reduction of the inorganic polluting load of vinasse/ optimize the use of vinasse culture medium for the growth of *S. maxima* |
| | Candido and Lombardi [105] | *Objective:* growth of microalgae (*Chlorella vulgaris*) on raw and biodigested sugarcane vinasse<br>*Motivation:* remediation of sugarcane vinasse (reduction of the eutrophication potential)/ characterization of the microalgae to encourage further research |
| | Santos et al. [109] | *Objective:* production of single-cell protein by growing *Candida utilis* CCT 3469 on vinasse from spirit (cachaça) production (replacing sugarcane molasses as the substrate)<br>*Motivation:* reduction of the organic polluting load of vinasse and assessment of an alternative low-cost feedstock to grow yeast |
| | Soto et al. [106] | *Objective:* growth of microalgae (*Chlorella vulgaris*) on raw sugarcane vinasse<br>*Motivation:* reduction of the organic polluting load of vinasse |
| Biochemicals production | Navarro et al. [73] | *Objective:* bioconcentration of sugarcane vinasse through recycling at the fermentation step (bioethanol production)<br>*Motivation:* reduce the consumption of energy at the step of concentration/ reduce the consumption of water and chemicals at the step of fermentation |
| | Kahraman and Gurdal [111] | *Objective:* laccase[b] production by white rot fungi (*Coriolus versicolor* and *Funalia trogii*) on natural culture medium with vinasse<br>*Motivation:* facilitate the implementation of laccase production by reducing production costs and reduce the polluting load of vinasse |
| | Pereira [126] | *Objective:* partial or total replacement of fresh water by vinasse (*in natura* and biologically treated) in the preparation of the yeast prior to fermentation<br>*Motivation:* reduce the polluting load of vinasse/ define an alternative approach to the management of sugarcane vinasse (environmentally-friendly technology) |
| | Aguiar et al. [54] | *Objective:* production of enzymes (laccase[b], peroxidase[c], and manganese-peroxidase[d]) by lignocellulolytic fungi (*Pleurotus sajor-caju* CCB020, *Pleurotus ostreatus*, *Pleurotus ostreatoroseus* CCB440, and *Trichoderma reesei*) from bagasse and vinasse<br>*Motivation:* aggregate value to the final production of sugarcane biorefineries through the exploitation of residual streams |

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| (Bio)technol. approach | Reference | Objective and motivation of the study |
|---|---|---|
| Biochemicals production | Menezes et al. [114] | *Objective:* assessment of the use of vinasse as a carbon source in the fermentation medium for spirits (cachaça) production<br>*Motivation:* propose an alternative use for vinasse |
| | Oliveira and Garcia-Cruz [55] | *Objective:* biosurfactant[e] production by *Bacillus pumilus* on sugarcane vinasse and waste frying oil<br>*Motivation:* stimulate the production of biosurfactants due to their environmental advantages/ reduce the production costs of biosurfactants by properly using residues |
| | Bastos et al. [113] | *Objective:* use of vinasse as a moistening agent for the solid-state cultivation of *Aspergillus niger* on sugarcane bagasse for citric acid production<br>*Motivation:* valuation of byproducts from sugarcane biorefineries/ improvement of the management of residues in biorefineries |
| | Colin et al. [112] | *Objective:* bioemulsifier[e] production by the actinobacterium *Streptomyces* sp. MCI on sugarcane vinasse<br>*Motivation:* reduce the polluting load of vinasse/ reduce the production costs of bioemulsifiers by using alternative substrates |
| | Madaleno et al. [127] | *Objective:* replacement of fresh water by vinasse (*in natura* and anaerobically treated) in the dilution of molasses prior to fermentation<br>*Motivation:* reduce the polluting load of vinasse combining different processes/ minimize the consumption of fresh water in the sugarcane processing chain |
| Agricultural application/ soil fertilization | Nandy et al. [133] | *Objective:* report the application of wastewater management approaches in a sugarcane biorefinery for bioresource recovery<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse (environmentally-friendly technology) |
| | Santos et al. [134] | *Objective:* development of a vinasse nutritive solution for hydroponics<br>*Motivation:* define a proper approach to the management of sugarcane vinasse (prevent negative effects) |
| | Gurgel et al. [132] | *Objective:* production of a granulated organomineral fertilizer from sugarcane residues (BIOFOM)<br>*Motivation:* define a proper approach to the management of sugarcane residues (environmentally-friendly technology) |

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| (Bio)technol. approach | Reference | Objective and motivation of the study |
|---|---|---|
| Soil remediation | Mariano et al. [138] | *Objective:* application of sugarcane vinasse as an amendment to ex-situ bioremediation of soil and groundwater contaminated with diesel oil<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse (environmentally-friendly technology) |
| | Crivelaro et al. [137] | *Objective:* application of sugarcane vinasse as a biostimulation agent for the biodegradation of oily sludge[f] in soil<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse/ optimize the landfarming systems usually employed in the treatment of oily-sludge |
| Energy production | Cortez and Pérez [136] | *Objective:* investigate the technical feasibility of on-site sugarcane vinasse combustion<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse (environmentally-friendly technology) |
| | Akram et al. [135] | *Objective:* investigate the potentials of sugarcane vinasse as a biofuel for combustion<br>*Motivation:* define an alternative approach to the management of sugarcane vinasse/ exploit the energy potential of vinasse |

Notes: [a]Single-cell protein comprises the protein obtained from the cultivation of microbial biomass, primarily used to supplement staple diets by replacing high-cost conventional protein sources, such as soymeal and fishmeal [290]. The use of low-cost substrates, such as residues from the agro-industry, is a key factor to enhance the economic feasibility of full-scale SCP production plants [108,290]. [b]Laccase plays an important role in the lignocellulolytic systems of fungi, acting specifically in the degradation of lignin [111]. The industrial applications for laccase are many, with emphasis on the degradation of the vegetable biomass prior to the application of bioprocesses. [c]Peroxidases form a group of oxidoreductases employed in the oxidation of a variety of organic and inorganic compounds [291]. The applications of peroxidases may include the manufacturing of reagents for clinical diagnosis, the degradation of phenolic compounds from wastewaters, and the removal of hydrogen peroxide ($H_2O_2$) from industrial effluents and foodstuffs [291]. Peroxidases are also involved in the degradation of lignin [54], which explains the production of this enzyme by lignocellulolytic fungi. [d]Manganese-peroxidase is an oxidoreductase which catalyzes the oxidation of manganese ($2Mn^{2+} + 2H^+ + H_2O_2 \leftrightarrow 2Mn^{3+} + 2H_2O$), also involved in the degradation of lignin. [e]Biosurfactants, bioemulsifiers, or natural emulsifiers are emulsifiers naturally produced (e.g. metabolites from microorganisms, such as glycolipids, lipopeptides, lipoproteins, phospholipids, fatty acids, and neutral lipids [55]), used to stabilize oil-in-water emulsions [292]. Oil-in-water emulsions are thermodynamically unstable, so that the application of (bio)emulsifiers reduces the interfacial tension between the oily phase and the water, and thus increases the kinetic stability of the emulsions [292]. Biosurfactants present a wide range of applications in pharmaceutical, cosmetic, and food industries [55,292], also with potential applications in the bioremediation of soils and sediments contaminated by organic and inorganic pollutants [112]. [f]The term oily sludge corresponds to the oily and viscous residues generated in the oil-based industries, such as in the steps of production and refining [137].

**Table S3.** Studies on the biodigestion of sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g L$^{-1}$) | Reactor(s) | Operating conditions | | |
| Russo et al. [175] | Juice | 21.5 | Single-phase (35°C) | OLR[a]: 1.2-3.4 | ER-COD[b]: 89.0-93.0 | · First report on the use of fixed-film reactors to sugarcane vinasse in Brazil |
| | | | APBR (21 L) | HRT: 15-6 days | MY[c]: 0.33-0.52 | · COD removal maintained at high levels (> 85%) despite the continuous increase in the OLR<br>· Drawback(s): unfavorable operating conditions for full-scale applications (low OLR and high HRT) |
| Costa et al. [174] | Juice | 33.0 | Single-phase (mesophilic) | OLR[a]: 18.3 | ER-COD[b]: 76.0 | · First report - in association with Craveiro et al. [34] - presenting experiences with the implementation of pilot-scale biodigestion plants to the processing of sugarcane vinasse in Brazil |
| | | | UASB (11 m$^3$) | HRT: 20 h | MY[c]: 0.28 | · Successful operation at a high[d] OLR and low[d] HRT<br>· Proposition of alternatives for the use of the biodigested vinasse |
| Craveiro et al. [34] | Juice | 31.3 | Single-phase (28-33°C) | OLR[a]: 13.2 | ER-COD[b]: 82.9 | · First techno-economic assessment for the implementation of full-scale biodigestion plants in sugarcane biorefineries |
| | | | UASB (11 m$^3$) | HRT: 2.4 days | MY[c]: 0.23 | · Successful operation at relatively[d] high OLR and low HRT |

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| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor(s) | Operating conditions | | |
| Souza et al. [37] | Juice + molasses | 31.5 | Single-phase (55-57°C) | OLR[a]: 26.5 | ER-COD[b]: 71.7 | · First case report on the application of thermophilic biodigestion to sugarcane vinasse in Brazil |
| | | | UASB (75 $m^3$) | HRT: 2 days | MY[c]: 0.22 | · Successful thermophilic pilot-scale operation at high[d] OLR and relatively low[d] HRT |
| | | | | | | · Minimal consumption of chemicals (4 g NaOH $kg^{-1}$COD) for pH adjustment[e] |
| | | | | | | · The operation of the reactor during the inter-harvest period was proposed |
| Döll and Foresti [59], Ribas [293] | Juice + molasses | 1.0-30.0 (diluted vinasse)[f] | Single-phase (35ºC) | OLR[a]: 2.5-35.9 | ER-COD[b]: 79.0-85.0[g] | · Mesophilic system: reduction in the $HCO_3^-$/COD ratio (1.0 to 0.2) maintaining high COD removal levels (~ 80%) |
| | | | ASBR (3.5 L) | HRT: 6-1 days (cycle time) | | |
| | | 1.0-20.0 (diluted vinasse)[f] | Single-phase (55°C) | OLR[a]: 2.5-5.7 | ER-COD[b]: 75.0[h] | · Thermophilic system: unstable performance; requirement of higher $HCO_3^-$/COD ratios (0.4-0.6) |
| | | | ASBR (3.5 L) | HRT: 1 day (cycle time) | | |
| | | | | | | · Drawback(s): dilution of vinasse associated to nutrient supplementation |

**Table S3.** Studies on the biodigestion of sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor(s) | Operating conditions | | |
| Mota et al. [177] | Juice | 15.5-17.7 | Two-phase (22ºC)<br>UAR[i] (6.7 L) + AnMBR[j] (24.0 L) | OLR[a]: 2.5<br>HRT: 5 days (AnMBR) | ER-COD[b]: 96.9 | · Proposition of a simple method for the start-up of methanogenic reactors: feeding reduction/interruption at VFA concentrations over 1,000 mg $L^{-1}$<br>· Drawback(s): unfavorable operating conditions for full-scale applications (low OLR and high HRT) |
| Siqueira et al. [60] | Juice + molasses | 2.3-20.1 (diluted vinasse)[k] | Single-phase (30°C)<br>AFBR (4.2 L) | OLR[a]: 3.3-26.2<br>HRT: 24 h | ER-COD[b]: 70.0[l]<br>MY[c]: 0.29 | · COD removal maximized at an OLR of 20 kg COD $m^{-3}$ $day^{-1}$ for a low HRT[d]<br>· Drawback(s): dilution of vinasse; the increase in the OLR negatively affected the COD removal associated to the accumulation of acids; high energy requirements for the fluidization of the bed [294] |
| Barros et al. [176] | Juice + molasses | 1.9-22.0 (diluted vinasse)[m] | Single-phase (mesophilic)<br>UASB (40.5L) | OLR[a]: 0.2-7.5<br>HRT: 2.8 days | ER-COD[b]: 67.0-49.0<br>MY[c]: 0.13-0.17 | · Effluent recirculation successfully replaced the addition of NaOH when the OLR was increased above 6-8 kg COD $m^{-3}$ $day^{-1}$: influent pH maintained in approximately 6.5-6.8 |

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| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor(s) | Operating conditions | | |
| Barros et al. [176] | Juice + molasses | 1.9-28.5 (diluted vinasse)[m] | Single-phase (mesophilic)<br>UASB (21.5 L) | OLR[a]: 0.2-11.5<br>HRT: 2.8-1.8 days | ER-COD[b]: 69.0-60.0<br>MY[c]: 0.14-0.11 | · Drawback(s): dilution of vinasse; the increase in the OLR reduced both the COD removal and methane yield (optimal values within the range of 2.5-5.0 kg COD $m^{-3}$ $day^{-1}$); relatively low OLR[n] |
| Ferraz Jr. et al. [35] | Juice + molasses | 35.2 (raw) | Single-phase (55ºC)<br>UASB (10 L) | OLR[a]: 15-25<br>HRT: 56-34 h | ER-COD[b]: 50.2-60.7<br>MY[c]: 0.18-0.23 | · COD removal and methane production maximized in the two-phase system at a high[d] OLR and low[d] HRT |
| | | 24.2 (acidified) | Two-phase (55ºC)<br>APBR[i] (2.3 L) + UASB[j] (3.4 L) | OLR[a]: 15-25<br>HRT: 39-23 h (UASB) | ER-COD[b]: 38.8-63.0<br>MY[c]: 0.23-0.31 | · Phase separation increased the bioenergy recovery and the anaerobic biodegradability of vinasse by 25.7% and 21%, respectively<br>· Phase separation reduced the $NaHCO_3$ demand by 50% (12.5 to 6.25 g $L^{-1}$) |
| Aquino et al. [33] | Juice + molasses | 6.0-18.0 (diluted vinasse)[o] | Single-phase (30°C)<br>APBR (2.7 L) | OLR[a]: 2.4-18.0<br>HRT: 60-24 h | ER-COD[b]: > 80.0[p]<br>MY[c]: 0.18-0.31 | · The structured-bed reactor (ASTBR) withstood higher OLR than the packed-bed one (APBR) maintaining high COD conversion without operating limitations (bed clogging) |

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| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor(s) | Operating conditions | | |
| Fuess et al. [36] | Juice + molasses | 28.3 (raw) | Two-phase (55ºC) | OLR[a]: 15-30 | ER-COD[b]: 55.1-73.9 (methanogenic phase) | · COD removal and methane production maximized at an OLR over 25 kg COD $m^{-3}$ $day^{-1}$ |
| | | 22.3 (acidified) | APBR[i] (2.3 L) + ASTBR[j] (2.5 L) | HRT: 37-18 h (ASTBR) | ER-COD[b]: 63.2-82.6 (global) | |
| | | | | | MY[c]: 0.25-0.30 | · The use of thermophilic methanogenic sludge acclimatized to sugarcane vinasse was imperative for achieving successful operation |
| Del Nery et al. [38] | - | 19.2 (raw) | Single-phase (22°C) | OLR[a]: 0.5-32.4 | ER-COD[b]: 87.5 | · Very small increments in the OLR (0.3 kg COD $m^{-3}$ $d^{-1}$) were imperative to achieve long-term (700 d) operating stability |
| | | | UASB (120 L) | HRT: 33.33-0.86 d | MY[c]: 0.30 | · High COD removal efficiency with OLR ca. 2-fold higher than the limiting value usually observed in UASB reactors (15.0 kg COD $m^{-3}$ $d^{-1}$) |

Notes: [a]Values in kg COD $m^{-3}$ $day^{-1}$. [b]Values in %. [c]Values in $m^3CH_4$ $kg^{-1}COD_{removed}$. [d]Compared to Russo et al. [175]. [e]An effluent recirculation ratio of 50% was applied to recycle the alkalinity generated in methanogenesis. [f]Raw vinasse: COD = 42-59 g $L^{-1}$. [g]COD removals for OLRs of 22.2-35.9 kg COD $m^{-3}$ $day^{-1}$; [h]COD removal for an OLR of 5.2 kg COD $m^{-3}$ $day^{-1}$. [i]Acidogenic reactor. [j]Methanogenic reactor. [k]Raw vinasse: COD = 36.0-49.0 g $L^{-1}$. [l]COD removal for an OLR of 20.0 kg COD $m^{-3}$ $day^{-1}$. [m]Raw vinasse: COD = 45 g $L^{-1}$. [n]Compared to Souza et al. [37], Ferraz Jr. et al. [35], and Fuess et al. [36]. [o]Raw vinasse: COD = 20.0-32.2 g $L^{-1}$. [p]Relative to the soluble COD and for OLR ≥ 10.2 kg COD $m^{-3}$ $d^{-1}$. [q]Relative to the soluble COD and for OLR ≥ 15.0 kg COD $m^{-3}$ $d^{-1}$.

Nomenclature - Reactors: AFBR = anaerobic fluidized-bed reactor; AnMBR = anaerobic membrane reactor; APBR = anaerobic packed-bed reactor; ASBR = anaerobic sequencing-batch reactor; ASTBR = anaerobic structured-bed reactor; UAR = upflow anaerobic reactor; UASB = upflow anaerobic sludge blanket reactor. Operating conditions: HRT = hydraulic retention time; OLR = organic loading rate. System performance: ER-COD = COD removal efficiency; MY = methane yield.

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| van Haandel and Catunda [46] | Electricity generation (non-defined prime mover - PMV) - η = 35% | Autonomous<br>Harvest: 200 days<br>PC: 120 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 20 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 25 g $L^{-1}$ | $Q_{CH4}$ = 100 kg $m^{-3}_{ethanol}$<br>LHV = 13.27 MCal $kg^{-1}$ (39.62 MJ $Nm^{-3}$) | *(1.9 MJ $L^{-1}_{ethanol}$)* |
| van Haandel [65] | Electricity generation (non-defined PMV) - η = 35-40% | Annexed[c]<br>SVP: 15 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 32 g $L^{-1}$ | $Q_{CH4}$ = 100 kg $m^{-3}_{ethanol}$ | **500 kWh $m^{-3}_{ethanol}$**<br>*(1.8 MJ $L^{-1}_{ethanol}$)* |
| Salomon and Lora [184] | Electricity generation in set of mGTBs (Ingersoll Rand) - η = 27%<br>Number of mGTBs: non-defined | Calculation for the total Brazilian ethanol production in the 2003/2004 harvest: 14,808,705 $m^3_{ethanol}$<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | - | $CH_4$ content: 60%<br>MY = 14.23 $m^3$ $m^{-3}_{vinasse}$<br>LHV = 20.09 MJ $Nm^{-3}$ | **819.27 MW**<br>*(1.04 MJ $L^{-1}_{ethanol}$)*[d] |
| | Electricity generation in set of ICEs (Brasmetano) - η = 29%<br>Number of ICEs: non-defined | Calculation for the total Brazilian ethanol production in the 2003/2004 harvest: 14,808,705 m³ethanol<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | - | $CH_4$ content: 60%<br>MY = 14.23 $m^3$ $m^{-3}_{vinasse}$<br>LHV = 20.09 MJ $Nm^{-3}$ | **879.96 MW**<br>*(1.12 MJ $L^{-1}_{ethanol}$)*[d] |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Rocha et al. [191] | Electricity generation in motor-generator sets: ICE Jenbacher (2.56 MW, η = 40%) + Wartsila (1.35 MW, η = 31%)<br><br>Number of ICEs: 2 Jenbacher + 1 Wartsila | Annexed<br>Harvest: 210 days<br>PC: 385.7 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 12 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 28.4 g $L^{-1}$ | $CH_4$ content: 60%<br>LHV = 18.2 MJ $kg^{-1}$ (20.02 MJ $Nm^{-3}$) | **16.82 kWh $m^{-3}_{vinasse}$**<br>*(0.73 MJ $L^{-1}_{ethanol}$)* |
| Salomon et al. [64] | Electricity generation in set of ICEs (Brasmetano, 250 kW) - η = 29%<br><br>Number of ICEs: 22 | Harvest: 180 days<br>PC: 500 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | COD[b] = 29 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.27 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.23 MJ $Nm^{-3}$ | **5.41 MW $harvest^{-1}$**<br>*(23,371 MWh $harvest^{-1}$)*<br>*(0.93 MJ $L^{-1}_{ethanol}$)* |
| | Electricity generation in set of mGTBs (Ingersoll Rand, 250 kW) - η = 32%<br><br>Number of mGTBs: 24 | Harvest: 180 days<br>PC: 500 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | COD[b] = 29 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.27 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.23 MJ $Nm^{-3}$ | **5.77 MW $harvest^{-1}$**<br>*(24,926 MWh $harvest^{-1}$)*<br>*(1.0 MJ $L^{-1}_{ethanol}$)* |
| Fuess and Garcia [62] | Electricity generation (non-defined PMV) - η = 30% | Autonomous[c]<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 30.4 g $L^{-1}$ | MY = 0.26 $Nm^3$ $kg^{-1}$COD<br>LHV = 9.136 kWh $m^{-3}$ = 32.9 MJ $m^{-3}$ | **0.83 MJ $L^{-1}_{ethanol}$** |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Fuess and Garcia [62] | Electricity generation (non-defined PMV) - η = 30% | Annexed[c]<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 45.8 g $L^{-1}$ | MY = 0.26 $Nm^3$ $kg^{-1}$COD<br>LHV = 9.136 kWh $m^{-3}$ = 32.9 MJ $m^{-3}$ | **1.25 MJ $L^{-1}_{ethanol}$** |
| Moraes et al. [63] | Electricity generation in set of ICEs (Caterpillar, Inc., model DM 5234, 50 Hz, 1500 rpm, 400 V) - η = 38% | Autonomous<br>Harvest: 167 days<br>PC: 992.8 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 21 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.5 MJ $Nm^{-3}$ | **27,400 MWh harvest$^{-1}$**<br>*(6.34 MW harvest$^{-1}$)*<br>*(0.55 MJ $L^{-1}_{ethanol}$)* |
| | Number of ICEs: non-defined | Annexed<br>Harvest: 167 days<br>PC: 639.5 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 9.8 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 33.6 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.5 MJ $Nm^{-3}$ | **27,500 MWh harvest$^{-1}$**<br>*(6.37 MW harvest$^{-1}$)*<br>*(0.86 MJ $L^{-1}_{ethanol}$)* |
| | Cogeneration of steam and electricity in industrial boilers (Siemens, model SGT 100, 4700 KW) - η = 30%<br>Number of boilers: non-defined | Autonomous<br>Harvest: 167 days<br>PC: 992.8 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 21 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.5 MJ $Nm^{-3}$ | **Electricity: 21,700 MWh harvest$^{-1}$**<br>*(5.02 MW harvest$^{-1}$)*<br>*(0.44 MJ $L^{-1}_{ethanol}$)* |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| **Reference** | **Biogas application** | **Assumptions for the estimates** | | | **Energetic potential**[a] |
|---|---|---|---|---|---|
| | | **Biorefinery** | **Vinasse** | **Biogas** | |
| Moraes et al. [63] | Cogeneration of steam and electricity in industrial boilers (Siemens, model SGT 100, 4700 KW) - η = 30%<br>Number of boilers: non-defined | Annexed<br>Harvest: 167 days<br>PC: 639.5 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 9.8 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 33.6 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}COD$<br>LHV = 21.5 MJ $Nm^{-3}$ | **Electricity: 21,800 MWh $harvest^{-1}$**<br>*(5.04 MW $harvest^{-1}$)*<br>*(0.68 MJ $L^{-1}_{ethanol}$)* |
| Fuess and Garcia [48] | Electricity generation (non-defined PMV) - η = 30% | Autonomous[c]<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 30.4 g $L^{-1}$ | MY = 0.28 $Nm^3$ $kg^{-1}COD$<br>LHV = 9.96 kWh $m^{-3}$ = 35.8 MJ $m^{-3}$ | **1.73 MJ $L^{-1}_{ethanol}$** |
| | | Annexed[c]<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 45.8 g $L^{-1}$ | MY = 0.28 $Nm^3$ $kg^{-1}COD$<br>LHV = 9.96 kWh $m^{-3}$ = 35.8 MJ $m^{-}$ | **2.61 MJ $L^{-1}_{ethanol}$** |
| Nogueira et al. [189] | Electricity generation in motor-generator set (ICE, 250 kW) - η = 23%<br>Number of ICEs: 4 | Autonomous<br>PC: 500 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 21 g $L^{-1}$ | $CH_4$ content: 60%<br>LHV = 6.5 kWh $m^{-3}$ = 23.4 MJ $m^{-3}$ | **75,000 kWh $d^{-1}$**<br>*(0.54 MJ $L^{-1}_{ethanol}$)* |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Albanez et al. [61] | non-defined | Annexed<br>Harvest: 253 days<br>PC: 596.4 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b,e] = 5.3 g $L^{-1}$ | MY = 9.47 mol $kg^{-1}$COD = 0.21 $Nm^3$ $kg^{-1}$COD<br>LHV = 890.36 kJ $mol^{-1}$ = 39.7 MJ $Nm^{-3}$ | **17 MW $harvest^{-1}$**<br>*(103,224 MWh $harvest^{-1}$)*<br>*(2.46 MJ $L^{-1}_{ethanol}$)* |
| Fuess and Garcia [187] | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = 43%<br>Number of ICEs: non-defined | Autonomous<br>Harvest: 232 days<br>PC: 1,429.3 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 30.4 g $L^{-1}$ | MY = 0.33 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.7 MJ $Nm^{-3}$ | **139,500 MWh $harvest^{-1}$**<br>**1.51 MJ $L^{-1}_{ethanol}$** |
| | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = 43%<br>Number of ICEs: non-defined | Annexed<br>Harvest: 232 days<br>PC: 920.7 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 45.8 g $L^{-1}$ | MY = 0.31 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.7 MJ $Nm^{-3}$ | **120,300 MWh $harvest^{-1}$**<br>**2.03 MJ $L^{-1}_{ethanol}$** |
| Bernal et al. [186] | Electricity generation in set of ICEs - η = 33%<br>Number of ICEs: non-defined | Autonomous<br>Planted area: 150,000 ha<br>SVP: 10-15 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 21.0 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.33 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.5 MJ $Nm^{-3}$ | **13.4 MW**<br>**96,607 MWh $year^{-1}$** |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| **Reference** | **Biogas application** | **Assumptions for the estimates** | | | **Energetic potential**[a] |
|---|---|---|---|---|---|
| | | **Biorefinery** | **Vinasse** | **Biogas** | |
| Bernal et al. [186] | Electricity generation in set of ICEs - η = 33% | Annexed | Juice + molasses | $CH_4$ content: 60% | **4.1 MW** |
| | | Planted area: 150,000 ha | COD[b] = 37.5 g $L^{-1}$ | MY = 0.33 $Nm^3$ $kg^{-1}$COD | **30,186 MWh $year^{-1}$** |
| | Number of ICEs: non-defined | SVP: 10-15 $L_{vinasse}$ $L^{-1}_{ethanol}$ | | LHV = 35.5 MJ $Nm^{-3}$ | |
| Fuess et al. [50] | Electricity generation and thermal energy recovery in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = variable according to the type of layout proposed for the biodigestion/power plant | Annexed | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 70% (two-phase system) | **Electricity: 7.0-7.5 MW (harvest) + 3.5-3.8 MW (inter-harvest)** |
| | | Harvest (200 days) + inter-harvest (130 days) | COD[f] = 22.3 g $L^{-1}$ (harvest) | MY = 0.301 $Nm^3$ $kg^{-1}$COD | *(0.56-0.60 MJ $L^{-1}_{ethanol}$; harvest)* |
| | | PC: 1,072.5 $m^3_{ethanol}$ $day^{-1}$ (harvest)/ 732.3 $m^3_{ethanol}$ $day^{-1}$ (inter-harvest) | COD[f] = 16.5 g $L^{-1}$ (inter-harvest) | | *(0.42-0.45 MJ $L^{-1}_{ethanol}$; inter-harvest)* |
| | | | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 58.4% (single-phase system) | **Electricity: 6.1 MW (harvest) + 2.8 MW (inter-harvest)** |
| | | SVP: 8.6 $L_{vinasse}$ $L^{-1}_{ethanol}$ | COD[b] = 28.3 g $L^{-1}$ (harvest) | MY = 0.234 $Nm^3$ $kg^{-1}$COD | *(0.49 MJ $L^{-1}_{ethanol}$; harvest)* |
| | Number of ICEs: non-defined | | COD[b] = 21 g $L^{-1}$ (inter-harvest) | | *(0.33 MJ $L^{-1}_{ethanol}$; inter-harvest)* |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Fuess et al. [50] | Electricity generation and thermal energy recovery in set of GTBs (Dresser-Rand, model KG2-3E) - η = variable according to the type of layout proposed for the biodigestion/power plant | Annexed | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 70% (two-phase system) | **Electricity: 7.5-7.9 MW (harvest) + 3.8-4.0 MW (inter-harvest)** |
| | | Harvest (200 days) + inter-harvest (130 days) | COD[f] = 22.3 g $L^{-1}$ (harvest) | MY = 0.301 $Nm^3$ $kg^{-1}$COD | *(0.61-0.64 MJ $L^{-1}_{ethanol}$; harvest)* |
| | | PC: 1,072.5 $m^3_{ethanol}$ $day^{-1}$ (harvest)/ 732.3 $m^3_{ethanol}$ $day^{-1}$ (inter-harvest) | COD[f] = 16.5 g $L^{-1}$ (inter-harvest) | | *(0.45-0.47 MJ $L^{-1}_{ethanol}$; inter-harvest)* |
| | | | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 58.4% (single-phase system) | **Electricity: 6.1 MW (harvest) + 3.0 MW (inter-harvest)** |
| | | SVP: 8.6 $L_{vinasse}$ $L^{-1}_{ethanol}$ | COD[b] = 28.3 g $L^{-1}$ (harvest) | MY = 0.234 $Nm^3$ $kg^{-1}$COD | *(0.49 MJ $L^{-1}_{ethanol}$; harvest)* |
| | Number of GTBs: non-defined | | COD[b] = 21 g $L^{-1}$ (inter-harvest) | | *(0.35 MJ $L^{-1}_{ethanol}$; inter-harvest)* |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | **Biorefinery** | **Vinasse** | **Biogas** | |
| Fuess et al. [50] | Electricity generation in set of GTBs (Dresser-Rand, model KG2-3E, η = variable according to the type of use layout for the biodigestion/power plant[e]) coupled to STBs (Siemens AG – Energy Sector – Oil & Gas Division, model SST-110, η = variable according to the type of layout proposed for the biodigestion/power plant) | Annexed | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 70% (two-phase system) | **Electricity: 10.3-10.8 MW (harvest) + 5.2-5.5 MW (inter-harvest)** |
| | | Harvest (200 days) + inter-harvest (130 days) | $COD^f$ = 22.3 g $L^{-1}$ (harvest) | MY = 0.301 $Nm^3$ $kg^{-1}COD$ | *(0.83-0.87 MJ $L^{-1}_{ethanol}$; harvest)* |
| | | PC: 1,072.5 $m^3_{ethanol}$ $day^{-1}$ (harvest)/ 732.3 $m^3_{ethanol}$ $day^{-1}$ (inter-harvest) | $COD^f$ = 16.5 g $L^{-1}$ (inter-harvest) | | *(0.61-0.65 MJ $L^{-1}_{ethanol}$; inter-harvest)* |
| | | | Juice + molasses (harvest)/ juice (inter-harvest) | $CH_4$ content: 58.4% (single-phase system) | **Electricity: 8.3 MW (harvest) + 4.0 MW (inter-harvest)** |
| | | SVP: 8.6 $L_{vinasse}$ $L^{-1}_{ethanol}$ | $COD^b$ = 28.3 g $L^{-1}$ (harvest) | MY = 0.234 $Nm^3$ $kg^{-1}COD$ | *(0.67 MJ $L^{-1}_{ethanol}$; harvest)* |
| | Number of GTBs/STBs: non-defined | | $COD^b$ = 21 g $L^{-1}$ (inter-harvest) | | *(0.48 MJ $L^{-1}_{ethanol}$; inter-harvest)* |
| Fuess and Zaiat [49] | Combined cycle (GTB + STB) - η = 56% | Autonomous | Juice | $CH_4$ content: 70% (two-phase system) | **13.4 MW $harvest^{-1}$** |
| | | Harvest: 200 days | $COD^b$ = 21 g $L^{-1}$ | MY = 0.301 $Nm^3$ $kg^{-1}COD$ | *(0.70 MJ $L^{-1}_{ethanol}$)* |
| | Number of GTBs/STBs: non-defined | PC: 1658 $m^3_{ethanol}$ $day^{-1}$ | | LHV = 23.8 MJ $Nm^{-3}$ | |
| | | SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | | | |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Fuess and Zaiat [49] | Combined cycle (GTB + STB) - $\eta$ = 56% | Annexed | Juice + molasses | $CH_4$ content: 70% (two-phase system) | **12.7 MW harvest$^{-1}$** |
| | | Harvest: 200 days | COD[b] = 30.9 g $L^{-1}$ | MY = 0.301 $Nm^3$ $kg^{-1}$COD | *(1.03 MJ $L^{-1}_{ethanol}$)* |
| | Number of GTBs/STBs: non-defined | PC: 1068 $m^3_{ethanol}$ $day^{-1}$ | | LHV = 23.8 MJ $Nm^{-3}$ | |
| | | SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | | | |
| Longati et al. [66] | Electricity generation in cogeneration plant (electric generator efficiency = 95.8%) | Autonomous | Juice | $CH_4$ content: 58.4% | **13.7 MWh harvest$^{-1}$** |
| | | Harvest: 232 days | COD[b] = 18.6 g $L^{-1}$ | MY = 0.234 $Nm^3$ $kg^{-1}$COD | *(0.0001 MJ $L^{-1}_{ethanol}$)* |
| | | PC: 1,779 $m^3_{ethanol}$ $day^{-1}$ | | Molar heating value ($CH_4$) = 802.9 kJ $mol^{-1}$ (35.85 MJ $Nm^{-3}$) | |
| | Number of boilers: non-defined | SVP: 8.14 $L_{vinasse}$ $L^{-1}_{ethanol}$ | | | |
| Santos et al. [78] | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - $\eta$ = 43% | Autonomous (entire Brazilian production) | Juice | MY = 0.328 $Nm^3$ $kg^{-1}$COD | **1,813 GWh harvest$^{-1}$** |
| | | Harvest: 232 days | COD[b] = 14.5 g $L^{-1}$ | LHV = 35.72 MJ $Nm^{-3}$ | *(0.82 MJ $L^{-1}_{ethanol}$)* |
| | | PC: 34,460 $m^3_{ethanol}$ $day^{-1}$ | | | |
| | Number of ICEs: non-defined | SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | | | |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Santos et al. [78] | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = 43%<br>Number of ICEs: non-defined | Annexed (entire Brazilian production)<br>Harvest: 232 days<br>PC: 85,192 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 13 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 35.4 g $L^{-1}$ | MY = 0.334 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.72 MJ $Nm^{-3}$ | **11,292 GWh $harvest^{-1}$**<br>*(2.06 MJ $L^{-1}_{ethanol}$)* |
| Pereira et al. [190] | Electricity generation in set of ICEs (no model specified) - η = 33%<br>Number of ICEs: non-defined | Annexed (645 municipalities in the State of São Paulo)<br>Harvest: 292 days[g]<br>SVP: 156 $L_{vinasse}$ $ton^{-1}_{cane}$ | Juice + molasses<br>COD[b] = 33.25 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.234 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.5 MJ $Nm^{-3}$ | **829 GWh $year^{-1}$** |
| Borges et al. [52] | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = 43%<br>Number of ICEs: non-defined | Annexed (entire Brazilian production)<br>Harvest: 200 days<br>PC: 178,386 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 27.7 g $L^{-1}$ | MY = 0.293 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.72 MJ $Nm^{-3}$ | **11.8 TWh $harvest^{-1}$**<br>*(1.19 MJ $L^{-1}_{ethanol}$)* |

**Table S4.** Estimates of the energetic potential of sugarcane vinasse targeting electricity production from biogas-$CH_4$. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | Energetic potential[a] |
|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | |
| Borges et al. [52] | Electricity generation in set of ICEs (GE Jenbacher GmbH & Co. OHG, model J620 GS-F12) - η = 43%<br>Number of ICEs: non-defined | Annexed<br>Harvest: 200 days<br>PC: 1,068 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 20.4 g $L^{-1}$ | MY = 0.293 $Nm^3$ $kg^{-1}$COD<br>LHV = 35.72 MJ $Nm^{-3}$ | **12.2 GWh harvest$^{-1}$**<br>*(0.20 MJ $L^{-1}_{ethanol}$)* |
| Moraes et al. [192] | Electricity generation in set of ICEs (Caterpillar, Inc., model DM 5234, 50 Hz, 1500 rpm, 400 V) - η = 38%<br>Number of ICEs: non-defined | Autonomous<br>Harvest: 200 days<br>PC: 1,700 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>VS[h] = 58 g $L^{-1}$ | $CH_4$ content: 85%<br>MY = 0.23 $Nm^3$ $kg^{-1}$VS<br>LHV = 10.02 kWh $Nm^{-3}$ (36.07 MJ $Nm^{-3}$) | **164.2 GWh harvest$^{-1}$**<br>*(1.74 MJ $L^{-1}_{ethanol}$)* |

Notes: [a]Values in **bold type** were reported in the studies; values in *italic type* were calculated from data presented in the studies for comparison purposes. [b]Raw vinasse (*in natura*). [c]Estimates based on energy balances for the production of 1$m^3$ of ethanol. [d]Considering a sugarcane harvesting period of 218 days [295]. [e]Diluted raw vinasse (~ 1:4). [f]Acidified vinasse. [g]Refers to the annual operating period of the biogas plant. [h]Volatile solids (VS) content considered in reactor feeding for a 80%:20% blend of vinasse and filter cake. 1 kWh = 3.6 MJ.

Nomenclature - Biogas application: PMV = prime mover; η = electric efficiency of the PMV; mGTB = microturbine (gas); ICE = internal combustion engine; GTB = gas turbine; STB = steam turbine. Biorefinery: SVP = specific vinasse production; PC = production capacity (distillery). Biogas: $Q_{CH4}$ = methane flow rate; MY = methane yield; LHV = lower heating value.

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Ferraz Jr. et al. [209] | Juice + molasses | 35.2 | Dark fermentation (55°C) | OLR[a]: 54.3-108.6 | ER-COD[b]: 26.2-33.3 | · Definition of an optimal OLR (mathematical fitting from experimental data) for the production of bio$H_2$ in a packed-bed reactor (84.2 kg COD $m^{-3}$ $day^{-1}$) |
| | | | APBR (2.3 L) | HRT: 24-8 h | VHPR[c]: 43.9-526.8 | |
| | | | | | HY[d]: 0.3-1.4 | |
| | | | | | HY[e]: 0.0-0.3 | · Molecular analyses indicated that the applied OLR strongly influences the microbial communities within the acidogenic reactors |
| | | | | | | · Drawback(s): HY considerably lower (0.3-1.4) than the theoretical value (8 mol $H_2$ $mol^{-1}_{sucrose}$) |
| Lazaro et al. [212] | Juice + molasses | 2.0-12.0 (diluted)[f] | Dark fermentation (37°C) Batch | Application of different initial COD values | HY[e]: 2.23 (maximum value) | · Increasing COD values negatively impacted the production of bio$H_2$ at thermophilic conditions |
| | | With nutrient supplementation | Dark fermentation (55°C) Batch | Application of different initial COD values | HY[e]: 2.31 (maximum value) | · Drawback(s): dilution of vinasse hampers full-scale applications |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Santos et al. [220] | Juice + molasses | 5.0 (diluted)[g]<br>With nutrient supplementation | Dark fermentation (55°C)<br>AFBR (2.6 L) | OLR[a]: 26.6-225.3 (vinasse + glucose)<br>HRT: 8-1 h | ER-COD[b]: < 20.0<br>VHPR[c]: 4,560-15,840<br>HY[e]: 4.98-1.97 | · Attainment of high VHPRs at low HRTs<br>· Acidified vinasse: high concentrations of potentially recoverable VFAs: butyric acid (up to 2,706 mg $L^{-1}$), succinic acid (up to 5,667 mg $L^{-1}$), and lactic acid (up to 1,358 mg $L^{-1}$)<br>· Drawback(s): dilution of vinasse coupled to the use of pure glucose (high costs); high energy requirements for the fluidization of the bed [294] |
| | | | | OLR[a]: 120.8-216.8 (vinasse)<br>HRT: 2-1 h | ER-COD[b]: < 20.0<br>VHPR[c]: 13,920-18,720<br>HY[e]: 3.53-2.06 | |
| Santos et al. [221] | Juice + molasses | 10.0 (diluted)[h]<br>With nutrient supplementation | Dark fermentation (55°C)<br>AFBR (2.6 L) | OLR[a]: 40.0-240.0<br>HRT: 6-1 h | ER-COD[b]: 8.5-13.5<br>VHPR[c]: 10,320-47,040<br>HY[e]: 2.86-1.92 | · Attainment of high VHPRs at low HRTs<br>· Long-term continuous bio$H_2$ production (150 days) |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Santos et al. [221] | Juice + molasses | 30.0<br>With nutrient supplementation | Dark fermentation (55°C)<br>AFBR (2.6 L) | OLR[a]: 120.0-720.0<br>HRT: 8-1 h | ER-COD[b]: 8.5-13.5<br>VHPR[c]: 7,680-19,440<br>HY[e]: 0.62-0.19 | · Acidified vinasse: high concentrations of potentially recoverable VFAs: butyric acid (1,067-4,813 mg $L^{-1}$), propionic acid (1,189-5,026 mg $L^{-1}$), and lactic acid (2,420-4,763 mg $L^{-1}$)<br><br>· Drawback(s): dilution of vinasse hampers full-scale applications; application of raw vinasse negatively impacted the production of bio$H_2$ (organic overloads); high energy requirements for the fluidization of the bed [294] |
| Santos et al. [222] | Juice + molasses | 15.0 (diluted)[i]<br>With nutrient supplementation | Dark fermentation (55°C)<br>AFBR (2.6 L) | OLR[a]: 60.0-360.0<br>HRT: 6-1 h | ER-COD[b]: 10.0-13.7<br>VHPR[c]: 10,800-35,760<br>HY[e]: 2.23-1.00 | · Attainment of high VHPRs at low HRTs<br>· Acidified vinasse: high concentrations of potentially recoverable VFAs: butyric acid (1,529-4,251 mg $L^{-1}$), propionic acid (1,236-4,378 mg $L^{-1}$), and lactic acid (1,025-3,822 mg $L^{-1}$) |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Santos et al. [222] | Juice + molasses | 20.0 (diluted)[j]<br>With nutrient supplementation | Dark fermentation (55°C)<br>AFBR (2.6 L) | OLR[a]: 80.0-480.0<br>HRT: 6-1 h | ER-COD[b]: 7.2-12.7<br>VHPR[c]: 12,960-28,800<br>HY[e]: 1.85-0.60 | · Drawback(s): dilution of vinasse hampers full-scale applications; application of raw vinasse negatively impacted the production of bio$H_2$ (organic overloads); high energy requirements for the fluidization of the bed [294] |
| Ferraz Jr. et al. [210] | Juice + molasses | 35.2 | Dark fermentation (55°C)<br>APBR (2.3 L) | OLR[a]: 84.2<br>HRT: 10.2 h | ER-COD[b]: 31.3<br>VHPR[c]: 762<br>HY[d]: 1.6<br>HY[e]: 1.10 | · Preliminary discussions on the impacts of biomass accumulation on bio$H_2$ production in acidogenic systems applied to sugarcane vinasse<br>· Bio$H_2$ production was improved (compared to Ferraz Jr. et al. [209]) by applying an optimal OLR<br>· Acidified vinasse: high concentrations of potentially recoverable VFAs: acetic acid (2,800 mg $L^{-1}$) and butyric acid (2,300 mg $L^{-1}$)<br>· Drawback(s): bio$H_2$ production ceased in a few days of operation (accumulation of biomass); HY considerably lower (1.6) than the theoretical value (8 mol $H_2$ $mol^{-1}_{sucrose}$) |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Ferraz Jr. et al. [211] | Juice + molasses | 35.2 | Dark fermentation (25°C)<br>APBR (2.3 L) | OLR[a]: 36.4<br>HRT: 24 h | ER-COD[b]: 37.3-40.1<br>VHPR[c]: 2.0-84.2<br>HY[d]: 0.01-0.6<br>HY[e]: 0.00-0.30 | · Definition of low-density polyethylene as the most appropriate material support for bio$H_2$ production in fixed-bed reactors<br>· Acidified vinasse: high concentrations of potentially recoverable VFAs: propionic acid (1,300-1,480 mg $L^{-1}$) and butyric acid (1,240-1,750 mg $L^{-1}$)<br>· Drawback(s): bio$H_2$ production ceased in a few days of operation; HY considerably lower (0.0-0.6) than the theoretical value (8 mol $H_2$ $mol^{-1}_{sucrose}$) |
| Lazaro et al. [213] | Juice + molasses | 15.0 (diluted)[k] (dark fermentation)<br>With nutrient supplementation | Dark-fermentation (30°C)<br>AFBR (1.4 L) | OLR[a] (AFBR): 120.0 (glucose + vinasse)<br>HRT (AFBR): 8 h | ER-COD[b] (AFBR): 16.5<br>HY[d] (AFBR): 0.47<br>HY[e] (AFBR): 0.34 | · Acidified vinasse (AFBR): high concentrations of potentially recoverable VFAs: butyric acid (3,700 mg $L^{-1}$) and propionic acid (2,000 mg $L^{-1}$) |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Lazaro et al. [213] | Juice + molasses | 1.8-11.7 (diluted)[l] (photo-fermentation) | Photo-fermentation (30°C): batch | Photo-fermentation: application of different initial COD values (acidified vinasse) | ER-COD[b] (photo-fermentation): 70.3-5.9 | · Drawback(s) (AFBR): dilution of vinasse hampers full-scale applications; high energy requirements for the fluidization of the bed [294]; HY considerably lower (0.47) than the theoretical value (8 mol $H_2$ $mol^{-1}_{sucrose}$) |
| | | | | | HY[m] (photo fermentation): 10.1-0.0 | · Drawback(s) (photo-fermentation): bio$H_2$ production severely hampered by increasing concentrations of vinasse (effects of toxic compounds and sulfate reduction); sulfide accumulation (up to 74.6 mg $L^{-1}$) at higher vinasse concentrations |
| Reis et al. [219] | Juice + molasses | 5.0 (diluted)[n] With nutrient supplementation | Dark fermentation (22°C) AFBR (1.4 L) | OLR[a]: 20.0 (vinasse + glucose) HRT: 6 h | VHPR[c]: < 4,800 HY[e]: 3.0-0.3 | · Establishment of methanogenesis when vinasse was used as the only carbon source negatively impacted bio$H_2$ production |
| | | | | OLR[a]: 20.0-120.0 (vinasse) HRT: 6-1 h | VHPR[c]: 0-14,400 HY[e]: 0.50-1.96 | · Enhanced production of methanol and ethanol at higher vinasse proportions |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Reis et al. [219] | Juice + molasses | 10.0 (diluted)[o]<br>With nutrient supplementation | Dark fermentation (22°C)<br>AFBR (1.4 L) | OLR[a]: 40.0 (vinasse + glucose)<br>HRT: 6 h | VHPR[c]: < 2,880<br>HY[e]: 1.2-0.80 | · Drawback(s): dilution of vinasse hampers full-scale applications; performance losses compared to other acidogenic AFBRs [220-222]; high energy requirements for the fluidization of the bed [294] |
| | | | | OLR[a]: 40.0-240.0 (vinasse)<br>HRT: 6-1 h | VHPR[c]: < 1,920<br>HY[e]: < 0.80 | |
| Fuess et al. [44] | Juice + molasses | 28.3 | Dark fermentation (55°C)<br>APBR (2.3 L) | OLR[a]: 84.2<br>HRT: 7.5 h | VHPR[c]: 1,203 (stable conditions)<br>HY[d]: 3.4 (stable conditions)<br>HY[e]: 0.87 (stable conditions) | · Demonstration of the capacity of acidogenic reactors to recover from performance losses through the implementation of operating strategies<br>· Establishment of long-term (240 days) production of bio$H_2$<br>· Definition of optimal conditions for the pH (5.1-5.2) and specific OLR (6.3-6.4 $g_{carbohydrates}$ $g^{-1}$VSS $day^{-1}$) for the production of bio$H_2$ from sugarcane vinasse in packed-bed reactors<br>· Drawback(s): HY lower (3.4) than the theoretical value (8 mol $H_2$ $mol^{-1}_{sucrose}$) |

**Table S5.** Studies on the production of $bioH_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Albanez et al. [208] | Juice + molasses | 6.0 (diluted)[p] | Dark fermentation (25°C)<br>AnSBBR (6.0 L) | OLR[a]: 6.9-20.6 (vinasse + molasses)<br>HRT: 3 h (cycle length) | ER-COD[b,q]: 13.0<br>VHPR[c,q]: 302 (OLR = 13.7 kg COD $m^{-3}$ $day^{-1}$)<br>HY[q,r]: 2.2 (OLR = 13.7 kg COD $m^{-3}$ $day^{-1}$) | · Co-digestion of vinasse and molasses positively affected the production of $bioH_2$: system stable, regardless of the operating conditions<br>· Proposition of a kinetic model considering the production of $bioH_2$ and VFAs (acetic, butyric, and valeric acids)<br>· Proposition of a full-scale acidogenic system: 6 parallel AnSBBRs (27,297 $m^3$ each) |
| Fuess et al. [77] | Juice + molasses | 19.5-49.0 | Dark fermentation (55°C)<br>ASTBR (1.9 L) | OLR[a]: 40.0-120.0<br>HRT: 24-4 h | VHPR[c,q]: 2074 (OLR = 87.5 kg COD $m^{-3}$ $day^{-1}$)<br>HY[q,r]: 15.6 (OLR = 87.5 kg COD $m^{-3}$ $day^{-1}$) | · Definition of an optimal OLR (mathematical fitting from experimental data) for the production of $bioH_2$ in a structured-bed reactor (70 kg COD $m^{-3}$ $day^{-1}$)<br>· Best performance regarding $bioH_2$ production in fixed-film reactors due to the bed configuration (improved biomass renewal)<br>· Prevailing pathways as function of the pH: lactate production (pH < 5.0), $bioH_2$/butyrate production (pH = 5.0-5.5) and $bioH_2$/butyrate production + sulfate reduction (pH > 6.0) |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Niz et al. [215] | Juice + molasses | 32.3 | Dark fermentation (70°C) | OLR[a]: 20.0-100.0 | VHPR[c,q]: 691 (OLR = 39.1 kg COD $m^{-3}$ $day^{-1}$) | · Extreme temperature inhibits the production of extracellular polymeric substances, preventing excess biomass accumulation and the subsequent performance losses |
| | | | ASTBR (3.0 L) | HRT: 19-8 h | HY[d,q]: 2.6 (OLR = 56 kg COD $m^{-3}$ $day^{-1}$) | · Long-term continuous bio$H_2$ production (295 days divided into two periods) was established without requiring operating strategies |
| Ramos and Silva [217] | Juice + molasses | 10.0 (diluted)[s] | Dark fermentation (55°C) | OLR[a]: 60.0 | VHPR[c]: 1,300 | · Long-term continuous stable (coefficient of variation = 12.3% for the VHPR) bio$H_2$ production (230 days) was established |
| | | With nutrient supplementation | AFBR (1,980 mL) | HRT: 4 h | HY[e]: 0.34 | · Bio$H_2$ losses due to propionate (13.2% of the metabolite distribution) and lactate (10.2%) accumulation were still observed<br>· Drawback(s): dilution of vinasse hampers full-scale applications; high energy requirements for the fluidization of the bed [294] |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
| --- | --- | --- | --- | --- | --- | --- |
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Rego et al. [218] | Juice + molasses | 5.0 (diluted)[t] | Dark fermentation (30°C) | OLR[a]: 15.0-120.0 | VHPR[c,q]: 800 (OLR = 60 kg COD $m^{-3}$ $day^{-1}$) | · Thermophilic conditions stimulated the establishment of bio$H_2$-producing pathways coupled to the production of ethanol, acetate and butyrate, whilst mesophilic conditions were associated with homoacetogenesis and propionate production (bio$H_2$ consumption) |
| | | With nutrient supplementation | AFBR (0.78 L) | HRT: 8-1 h | HY[e,q]: 0.27 (OLR = 60 kg COD $m^{-3}$ $day^{-1}$) | |
| | | | Dark fermentation (55°C) | OLR[a]: 15.0-120.0 | VHPR[c,q]: 6420 (OLR = 60 kg COD $m^{-3}$ $day^{-1}$) | · Drawback(s): dilution of vinasse hampers full-scale applications; high energy requirements for the fluidization of the bed [294] |
| | | | AFBR (0.78 L) | HRT: 8-1 h | HY[e,q]: 1.06 (OLR = 60 kg COD $m^{-3}$ $day^{-1}$) | |
| Piffer et al. [79] | Juice + molasses | 18.9-28.1 | Dark fermentation (55°C) | OLR[a]: 30.0-90.0 | VHPR[c,q]: 401 (OLR = 68.3 kg COD $m^{-3}$ $day^{-1}$) | · High sodium concentrations in vinasse were demonstrated to naturally maintain high pH values during fermentation (>6.0), stimulating the metabolism sulfate-reducing bacteria without the addition of external alkalizing agents |
| | | | ASTBR (1.9 L) | HRT: 24-6 h | HY[q,r]: 2.1 (OLR = 68.3 kg COD $m^{-3}$ $day^{-1}$) | · Sulfate removal was coupled to acetate accumulation, characterizing a highly suitable fermented substrate for further processing towards methane production |

**Table S5.** Studies on the production of $bioH_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Piffer et al. [79] | | | | | | · The uptake of lactate was demonstrated to depend on the prevailing pH: electron donor in sulfidogenesis (pH > 6.0) or substrate in chain elongation towards butyrate and caproate production (pH 5.0-6.0) |
| Bernal et al. [214] | Juice + molasses | 10.0 (diluted)[u] | Dark fermentation (30°C) | OLR[a]: 10.0-240.0 | No $bioH_2$ detected, regardless of the operating condition | · The hydrogenogenic activity was not favored when using highly (COD = 10 g $L^{-1}$) to moderately (COD = 20 g $L^{-1}$) diluted vinasse in OLR < 480 kg COD $m^{-3}$ $day^{-1}$. Acetate (due to homoacetogenesis) and propionate prevailed in such conditions |
| | | With nutrient supplementation | EGSB (1,961 mL) | HRT: 24-1 h | | |
| | | 20.0 (diluted)[u] | Dark fermentation (30°C) | OLR[a]: 20.0-480.0 | VHPR[c]: 4,360 (OLR = 480 kg COD $m^{-3}$ $day^{-1}$) | · Extremely high OLR enhanced vinasse acidification; however, the detection of high propionate and lactate concentrations (along with butyrate) indicated the occurrence of $bioH_2$ losses |
| | | With nutrient supplementation | EGSB (1,961 mL) | HRT: 24-1 h | HY[e]: 0.34 (OLR = 480 kg COD $m^{-3}$ $day^{-1}$) | |

**Table S5.** Studies on the production of bio$H_2$ from sugarcane vinasse in Brazil. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Vinasse characterization | | System description | | System performance | Remarks |
|---|---|---|---|---|---|---|
| | Feedstock | COD (g $L^{-1}$) | Reactor | Operating conditions | | |
| Bernal et al. [214] | Juice + molasses | 30.0 (diluted)[u] | Dark fermentation (30°C) | OLR[a]: 30.0-720.0 | VHPR[c]: 8,770 (OLR = 720 kg COD $m^{-3}$ $day^{-1}$) | · Drawback(s): dilution of vinasse hampers full-scale applications |
| | | With nutrient supplementation | EGSB (1,961 mL) | HRT: 24-1 h | HY[e]: 0.33 (OLR = 480 kg COD $m^{-3}$ $day^{-1}$) | |

Notes: [a]Values in kg COD $m^{-3}$ $day^{-1}$. [b]Values in %. [c]Values in mL $H_2$ $L^{-1}$ $day^{-1}$. [d]Values in mol $H_2$ $mol^{-1}_{carbohydrates}$. [e]Values in mmol $H_2$ $g^{-1}COD_{influent}$. [f]Raw vinasse: COD = 32.0 g $L^{-1}$. [g]Raw vinasse: COD = 30.4-33.8 g $L^{-1}$. [h]Raw vinasse: COD = 30.0 g $L^{-1}$. [i]Raw vinasse: COD = 30.4-33.0 g $L^{-1}$. [j]Raw vinasse: COD = 30.4-33.0 g $L^{-1}$. [k]Raw vinasse: COD non-available . [l]Acidified effluent (glucose + vinasse): COD = 12.5 g $L^{-1}$. [m]Value in mmol $H_2$ $g^{-1}COD_{removed}$. [n]Raw vinasse: COD = 42.8 g $L^{-1}$. [o]Raw vinasse: COD = 42.8 g $L^{-1}$. [p]Raw vinasse: COD = 25 g $L^{-1}$; molasses: COD = 1,100 g $L^{-1}$. [q]Optimal values. [r]Value in mmol $H_2$ $g^{-1}$carbohydrates. [s]Raw vinasse: COD = 32.0 g $L^{-1}$. [t]Raw vinasse after physicochemical pretreatment with CaO: COD = 27.8 g $L^{-1}$. [u]Raw vinasse: COD = 32.0 g $L^{-1}$.

Nomenclature - Reactors: AFBR = anaerobic fluidized-bed reactor; AnSBBR = anaerobic sequencing batch biofilm reactor; APBR = anaerobic packed-bed reactor; ASTBR = anaerobic structured-bed reactor; EGSB = expanded granular sludge bed. Operating conditions: HRT = hydraulic retention time; OLR = organic loading rate. System performance: ER-COD = COD removal; VHPR = volumetric hydrogen production rate; HY = hydrogen yield.

**Table S6.** Estimates of the potential production and application of bio$CH_4$ in Brazilian sugarcane biorefineries. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text.

| Reference | Biogas application | Assumptions for the estimates | | | | Remarks |
|---|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | Bio$CH_4$ | |
| Souza et al. [268] | Bio$CH_4$ production and further use as fuel in urban buses (diesel replacement) | Harvest: 200 days<br>MC: 40,000 TC $day^{-1}$<br>PC: 2,060.0 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | - | $CH_4$ content: 50%<br>BY = 0.45 $Nm^3$ $kg^{-1}COD$<br>$Q_{biogas}$ = 146.0 $Nm^3$ $m^{-3}_{ethanol}$ | $Q_{bioCH4}$ = 52.1 $Nm^3$ $m^{-3}_{ethanol}$ | · Buses[a] supplied with bio$CH_4$: 788-214 (depending on the size of the biorefinery)<br>· Wider analysis: 50% of the Brazilian bus fleet (52,643) could be supplied with the bio$CH_4$ produced from the entire volume of vinasse produced in Brazil (2008/2009 harvest) |
| | | Harvest: 200 days<br>MC: 12,500 TC $day^{-1}$<br>PC: 558.1 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | - | $CH_4$ content: 50%<br>BY = 0.45 $Nm^3$ $kg^{-1}COD$<br>$Q_{biogas}$ = 146.0 $Nm^3$ $m^{-3}_{ethanol}$ | $Q_{bioCH4}$ = 52.1 $Nm^3$ $m^{-3}_{ethanol}$ | |
| Moraes et al. [63] | Biogas (considering only the removal of $H_2S$) production and further use as alternative vehicular fuel | Autonomous<br>Harvest: 167 days<br>MC: 11,976 TC $day^{-1}$<br>PC: 992.8 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD = 21 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}COD$<br>LHV = 21.5 MJ $Nm^{-3}$ | - | · Potential diesel displacement[b]: 8,000 $m^3$ (supplied fleet: 419-422 heavy-duty trucks[c])<br>· Potential gasoline displacement[d]: 8,900 $m^3$ (supplied fleet: 12,700-12,800 flex-fuel cars[e]) |

**Table S6.** Estimates of the potential production and application of bio$CH_4$ in Brazilian sugarcane biorefineries. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | | Remarks |
|---|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | Bio$CH_4$ | |
| Moraes et al. [63] | Biogas (considering only the removal of $H_2S$) production and further use as alternative vehicular fuel | Annexed<br>MC: 11,976 TC $day^{-1}$<br>Harvest: 167 days<br>PC: 639.5 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 9.8 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD = 33.6 g $L^{-1}$ | $CH_4$ content: 60%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 21.5 MJ $Nm^{-3}$ | - | · Potential ethanol displacement[f]: 11,500 $m^3$ (supplied fleet: 11,000 flex-fuel cars[g])<br>· Effective[h] reduction on diesel consumption in distilleries: 40% (remaining biogas used in the cogeneration system to produce 2,600 MWh monthly) |
| Junqueira et al. [267] | Bio$CH_4$ production and further use as alternative vehicular fuel (diesel replacement) | Annexed<br>MC: 20,000 TC $day^{-1}$<br>Harvest: 200 days<br>PC: 1,074.0 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 8.5 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD = 33.6 g $L^{-1}$ | $CH_4$ content: 76%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 27.3 MJ $Nm^{-3}$<br>$Q_{biogas}$ = 102.2 $Nm^3$ $m^{-3}_{ethanol}$ | $CH_4$ content: 96.5%<br>LHV = 30.5 MJ $Nm^{-3}$<br>$Q_{bioCH4}$ = 80.5 $Nm^3$ $m^{-3}_{ethanol}$ | · 16.7% reduction[i] in the production cost of sugarcane (USD 27.90 $TC^{-1}$ to USD 23.22 $TC^{-1}$)<br>· 40.0% increase[i] in the net present value of the biorefinery project (USD 135 million to USD 189 million)<br>· 7.5% increase[i] in the internal rate of return (16.0% to 17.2%) |

**Table S6.** Estimates of the potential production and application of bio$CH_4$ in Brazilian sugarcane biorefineries. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | | Remarks |
|---|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | BioCH4 | |
| Junqueira et al. [267] | Bio$CH_4$ production and further sale to the natural gas grid[i] | Annexed<br>MC: 20,000 TC $day^{-1}$<br>Harvest: 200 days<br>PC: 1,074.0 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 8.5 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD = 33.6 g $L^{-1}$ | $CH_4$ content: 76%<br>MY = 0.29 $Nm^3$ $kg^{-1}$COD<br>LHV = 27.3 MJ $Nm^{-3}$<br>$Q_{biogas}$ = 102.2 $Nm^3$ $m^{-3}_{ethanol}$ | $CH_4$ content: 96.5%<br>LHV = 30.5 MJ $Nm^{-}$<br>$Q_{bioCH4}$ = 80.5 $Nm^3$ $m^{-3}_{ethanol}$ | · 28.1% increase[i] in the net present value of the biorefinery project (USD 135 million to USD 173 million)<br>· 5.0% increase[i] in the internal rate of return (16.0% to 16.8%) |
| Fuess and Zaiat [49] | Bio$CH_4$ production and further sale to the natural gas grid[i] | Autonomous<br>Harvest: 200 days<br>PC: 1658 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>COD[b] = 21 g $L^{-1}$ | $CH_4$ content: 70% (two-phase system)<br>MY = 0.301 $Nm^3$ $kg^{-1}$COD<br>LHV = 23.8 MJ $Nm^{-3}$ | $CH_4$ content: 96.5%<br>LHV = 32.5 MJ $Nm^{-3}$ | · Bioenergy production (as bio$CH_4$) in the ranges of 15.0-20.0 MW and 20.0-25 MW in single- and two-phase AD plants, respectively |
| | | Annexed<br>Harvest: 200 days<br>PC: 1068 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice + molasses<br>COD[b] = 30.9 g $L^{-1}$ | $CH_4$ content: 70% (two-phase system)<br>MY = 0.301 $Nm^3$ $kg^{-1}$COD<br>LHV = 23.8 MJ $Nm^{-3}$ | $CH_4$ content: 96.5%<br>LHV = 32.5 MJ $Nm^{-3}$ | · Annual diesel savings ranging from 15.2 to 36.0 million liters depending on the type of truck |

**Table S6.** Estimates of the potential production and application of bio$CH_4$ in Brazilian sugarcane biorefineries. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | | Remarks |
|---|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | Bio$CH_4$ | |
| Fuess and Zaiat [49] | | | | | | · Competitive bio$CH_4$ production costs (0.08-0.10 USD $Nm^{-3}$) due to considering the use of in situ microaeration ($H_2S$ removal) coupled to organic solvent scrubbing ($CO_2$ removal) |
| Moraes et al. [192] | Bio$CH_4$ production and further sale to the natural gas grid or alternative vehicular fuel (diesel replacement) | Autonomous<br>Harvest: 200 days<br>PC: 1,700 $m^3_{ethanol}$ $day^{-1}$<br>SVP: 10 $L_{vinasse}$ $L^{-1}_{ethanol}$ | Juice<br>$VS^h$ = 58 g $L^{-1}$ | $CH_4$ content: 85%<br>MY = 0.23 $Nm^3$ $kg^{-1}$VS<br>LHV = 10.02 kWh $Nm^{-3}$ (36.07 MJ $Nm^{-3}$) | $CH_4$ content: 96.5%<br>$Q_{bioCH4}$ = 39×10$^6$ $Nm^3$ $harvest^{-1}$ | · Potential diesel displacement of 30.2×10$^3$ $m^3$ per harvest<br>· Internal rate of return values of ca. 25% and 40% when considering biogas injection into the gas grid and diesel replacement, respectively, corresponding to values at least 60% than the ones estimated for electricity generation (ca. 15%) |

**Table S6.** Estimates of the potential production and application of $bioCH_4$ in Brazilian sugarcane biore-fineries. The studies are organized chronologically. Bibliographic details of the references cited herein can be found in the main text (continued).

| Reference | Biogas application | Assumptions for the estimates | | | | Remarks |
|---|---|---|---|---|---|---|
| | | Biorefinery | Vinasse | Biogas | $BioCH_4$ | |
| Moraes et al. [192] | | | | | | · Net present value of USD 185 mi associated to diesel replacement (almost 3-fold higher than $bioCH_4$ injection into the gas grid) |

Notes: [a]Autonomy = 400 km with compressed natural gas cylinders of 1.055 $m^3$; specific diesel consumption = 0.40 L $km^{-1}$. [b]1.0 $Nm^3_{biogas}$ = 0.55 $L_{diesel}$. [c]Engine performance: 3.2 km $L^{-1}$. [d]1 $Nm^3_{biogas}$ = 0.61 $L_{gasoline}$. [e]Engine performance: 12.0 km $L^{-1}$. [f]1 $Nm^3_{biogas}$ = 0.79 $L_{ethanol}$. [g]Engine performance: 8.0 km $L^{-1}$. [h]The use of non-purified biogas, i.e., without $CO_2$ removal, demands the supplementation of heavy-duty engines (trucks) with diesel to maintain the conversion efficiency of the engine. [i]Compared to a biorefinery without considering the biodigestion of vinasse, .i.e., raw vinasse directed to fertirrigation. [j]Considering an average distance of 3 km betweeen the biorefinery and the gas grid.

Nomenclature - Biorefinery: MC = milling capacity (sugarcane mill); SVP = specific vinasse production; PC = production capacity (distillery); TC = ton of cane. Biogas: BY = biogas yield; $Q_{biogas}$ = biogas flow rate; MY = methane yield; LHV = lower heating value. $BioCH_4$: $Q_{bioCH4}$ = biomethane flow rate.