Assessing the economic and environmental sustainability of bio-olefins: The case of 1,3-butadiene production from bioethanol

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ABSTRACT

There is a growing interest in the production of biobutadiene from bioethanol, but it is not possible to conclude from the literature which conversion process, either by one or two reaction steps, is preferred since there is a lack of works comparing their economic and environmental performances. The aim of this work is to perform that comparison so it can serve as a guide for decision making by future investors as well as set future research needs that can improve the technology. Assuming production in Brazil from sugarcane ethanol, technoeconomic and lifecycle assessments were performed from process simulations, and the reliability of the results was studied with uncertainty analyses. The comparison reveals that the one-step process should be preferred because of its better economic and environmental performance. Biobutadiene from ethanol is not cost competitive against naphtha-derived butadiene (probability of positive net present value is 11–17% for one-step process scenarios and 5% for the two-step process scenarios) but producing biobutadiene from ethanol in Brazil leads to significant reductions in emissions of CO_2 compared to naphta-derived butadiene (102–103% and 7.6–52.4% for one- and two-step process scenarios, respectively). A critical issue for the cost competitiveness of biobutadiene is that the CO_2 saved can be sold in an international carbon emission trading market. In that case, the one-step processes would be much more favored. Future research is needed concerning the development of highly selective two-step catalysts operating in less energy-demanding conditions so that two-step processes can compete with one-step processes.

1. Introduction

In the petrochemical sector, 1,3-butadiene (1,3-BD) is one of the most important olefins, along with ethylene and propylene, and it is a building block for producing elastomers, resins, and synthetic rubbers with a large variety of uses such as tires for the automotive industry, sealants, clothing, and plastic casings for electronic products (Statista, 2017). Most 1,3-BD (95%) is produced as a byproduct of ethylene manufacturing through naphtha steam cracking, while a small fraction of 1,3-BD is produced deliberately by the dehydrogenation of n-butene and n-butane (Angelici et al., 2013).

The shift from oil-derived feedstocks (Ren et al., 2008) to renewable feedstocks for 1,3-BD production is appealing to reduce the environmental impact (Panahi et al., 2019). This has brought attention again to the catalytic production of 1,3-BD from bioethanol, a technology that was abandoned in the 1960s after cheaper naphtha-derived 1,3-BD became available. Two industrial production processes were developed: the one-step and the two-step reaction process. In both processes, the same reaction pathway is followed for the conversion of bioethanol to 1,3-BD, but in the two-step process, the conversion is performed in two separate stages: in the first reactor, acetaldehyde is produced by ethanol dehydrogenation (Eq. (1)), and in the second reactor, the mixture of acetaldehyde and ethanol is converted into 1,3-BD (Eq. (2)). The overall reaction (Eq. (3)) indicates a stoichiometric mass yield of 0.587 kg 1,3-BD per kg of ethanol. Lower 1,3-BD yields than the stoichiometric yield are actually achieved since side products are formed (Pomalaza et al., 2020), for example diethyl ether, ethylene, n-butanol, butenes, and heavy products (C_{6+}).

$$C_2H_6O \rightarrow C_2H_4O + H_2 \qquad \text{Eq. 1}$$

$$C_2H_6O + C_2H_4O \rightarrow C_4H_6 + 2H_2O \qquad \text{Eq. 2}$$

Abbreviations

1,3-BD	1,3-butadiene
CAPEX	Capital expenditure
CED	Cumulative energy demand
CHP	Combined heat and power
DMF	Dimethylformamide
ETB	Ethanol to butadiene
GWP100	Global warming potential over 100 years
HEN	Heat exchange network
HPS	High-pressure steam
IRR	Internal rate of return
LCA	Lifecycle assessment
LPS	Low-pressure steam
MBSP	Minimum butadiene selling price
MPS	Medium-pressure steam
NPV	Net present value
OPEX	Operating expenditure
ROI	Return on investment
TEA	Techno-economic assessment
WC	Water consumption
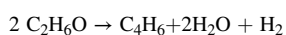
$$2 \, C_2H_6O \rightarrow C_4H_6 + 2H_2O + H_2 \qquad \text{Eq. 3}$$

The conversion in two steps allows achieving high selectivity by using a tailored catalyst and choosing optimal reaction conditions for each conversion step. It cannot be concluded from the literature (Rodgers et al., 2022) whether the two-step process should be preferred over the one-step process. The reason is that all published works except one (Cespi et al., 2016) have studied only one of the two processes, and it is difficult to compare their results since their assumptions differ substantially (Table 1) regarding the following: (i) starting raw material (C_6 sugars, cereal crops, biomass residues, and black liquor); (ii) process design decisions such as final use of byproducts (as fuel in the plant or sold as chemicals) and power and heat integration of the plant (as a stand-alone plant with its own CHP system or as a processing area within a biorefinery with a shared CHP system); (iii) plant location and production capacity (ranging from 24 to 200 kt/y); and (iv) databases and methodologies for technoeconomic and lifecycle assessments (TEA and LCA, respectively).

Only one study (Cespi et al., 2016) compared both processes, and the authors concluded that the two-step process was less economically and environmentally sustainable than the one-step process. This conclusion must be interpreted cautiously because the authors decided that unconverted reactants from the reactor were burnt as fuels rather than recovered and recycled to the reactor as usual. This disfavored the two-step process, whose consumption of ethanol per ton of 1,3-BD was twice the consumption of the one-step process. This is counterintuitive since in their study the two-step catalyst was more selective to 1,3-BD. As ethanol was the main contributor to production costs and environmental burdens, the two-step process was found less sustainable.

The novelty of the present work is that it rigorously compares the environmental and economic performances of one and two-step processes by applying the same methodology and assumptions in the TEA and LCA for a fair comparison, with the aim to fill the gap identified in the literature and provide insight into what process should be preferred. This is the first time that a statistical comparison of the economic and environmental performances of the one- and two-step processes has been carried out. The findings of this work can serve as a guide for the decision making of future investors by revealing the relative advantages and disadvantages of each process, and they set future research needs so this technology can again reach commercial status.

2. Materials and methods

Four scenarios were studied to compare the production of 1,3-BD from bioethanol by one (B1 and B2 scenarios) and two reaction steps (B3 and B4 scenarios). In the B1 and B3 scenarios the one- and two-step processes, respectively, were conceptually designed from the performance data of one- (Cabello González et al., 2019) and two-step (Cabello González et al., 2022) catalysts with high yield selected from the literature. Performance data were obtained from catalytic tests in our laboratory in which the effect of reaction products and ethanol impurities in the reactor feed were accounted for to model the reactor performance more realistically and achieve accurate TEA and LCA results. To evaluate the impact of catalyst selectivity in the TEA and LCA, an additional scenario was considered for each process (B2 and B4 for the one- and two-step process, respectively) by using performance data of other highly selective catalysts from the literature (Section 2.2). In all scenarios the processes were designed for a production capacity of 200 kt/y of 1,3-BD. The simulation of the processes provided the mass and energy balances for the TEA and LCA. In the case of the production process of 1,3-BD from naphtha, the built-in model in the Ecoinvent (V3) database was used to extract that information for the LCA (Ecoinvent Centre, 2018).

The design and simulation of the one-step process was presented in a previous work by Cabrera Camacho et al. (2020) from which the energy and mass balances for scenarios B1 and B2 were taken. The design of the two-step process (Section 2.1) and the mass and energy balance of scenarios B3 and B4 (Section 3.1) are presented in this work. The methodologies and assumptions of the TEA and LCA applied to both processes are described in Sections 2.3 and 2.4. Stochastic analyses were carried out in the TEA and LCA to assess the impact of uncertainty in the input data regarding the reliability of the results. For the study, Brazil was chosen as the plant location since based on our previous work on the one-step process, this location resulted in the best environmental performance compared to other major ethanol-producer regions (Europe and the US).

2.1. Description of the two-step process

The hierarchical method of Douglas (Dimian, 2003) was followed for the conceptual design of the overall process, while the method of Barnicki and Fair (Barnicki and Fair, 1990, 1992) was specifically followed for the design of the separation section. The plant is assumed to be stand alone, but it is adjacent to a petrochemical complex to which it can sell the produced 1,3-BD and coproducts. A simplified block diagram of the resulting two-step process is shown in Fig. 1, and it is briefly described in this subsection. A more detailed flow diagram and description of the process are provided in Appendix B.

An ethanol recycle stream that has been purified but still contains mainly water (7.5 wt%) as impurity is vaporized and fed to the dehydrogenation furnace reactor (reaction and separation 1, Fig. 1). The condensable species (mostly acetaldehyde, water, and unreacted ethanol) in the reactor effluent are separated from hydrogen based on a large difference in volatility. Hydrogen with high purity (99.9 mol%) is recovered and sold as a byproduct. The condensable fraction from the dehydrogenation reactor effluent is mixed with an acetaldehyde recycle stream, resulting in an aqueous ethanol/acetaldehyde mixture (7.5 wt% water) that constitutes the feed to the second furnace reactor. The condensable fraction (unreacted ethanol and acetaldehyde, water, acetone, butanal, diethyl ether, and heavy compounds) and gases (butenes, propylene, ethylene, and 1,3-BD) from the second reactor are separated based on large differences in volatility. The stream of gases is scrubbed with fresh ethanol (7.5 wt% water, ethanol feed to reaction and separation 2, Fig. 1) to recover 1,3-BD. The ethanol containing the recovered 1,3-BD is mixed with the condensable fraction of the second reactor, which contains a substantial amount of 1,3-BD. This mixture is separated by distillation to obtain crude butadiene with a relatively high

Table 1
Published works on TEA and LCA of the ethanol-to-butadiene (ETB) processes.

| Work	Route	Starting raw material	Plant location	Process design and modelling	TEA	LCA	Main conclusions
Cespi et al. (2016)	One- and two-step	Anhydrous first-generation ethanol from regional crops	US, Europe, Brazil	Catalyst performance data from patents. Simple process modelling by stoichiometric balances. Combustion of unconverted reactants and byproducts.	Deterministic. Relative economic assessment based on economic index (ratio of BD price/cost of raw material and utilities). Production capacity unknown. Economic assessment not performed. Production capacity: 200 kt/y butadiene.	Deterministic. Cradle to gate. GWP, WC, and CED impacts. Comparison with naphtha-cracking route. LCA modelling with SimaPro software and ecoinvent database.	Better environmental performance of one-step process than two-step process and naphtha-cracking route for all plant locations.
Shylesh et al. (2016)	One-step	Anhydrous ethanol from the US (corn-grain or corn-stover ethanol) or imported from Brazil (sugarcane ethanol)	US	Catalyst performance data from catalytic tests by authors. Process modelling in Aspen Plus. Plant as add-on to existing bioethanol plant. Byproducts are sold.	Deterministic. Relative economic assessment based on economic index (ratio of BD price/cost of raw material and utilities). Production capacity unknown. Economic assessment not performed. Production capacity: 200 kt/y butadiene.	Deterministic. Cradle to grave. Only GWP impact. Comparison with naphtha-cracking route. LCA software not disclosed. Emission factors taken from literature.	Only butadiene derived from corn-stover ethanol or sugarcane ethanol has lower GWP than naphtha-derived butadiene.
Farzad et al. (2017)	Two-step	Azeotropic ethanol from sugarcane bagasse and harvesting residue	South Africa	Catalyst performance data from industrial catalysts. Process modelling in Aspen Plus. Simulation of bioethanol and butadiene plant with common CHP system. Two scenarios: (i) self-sufficient energy plant and (ii) import of coal. Byproducts are burnt.	Stochastic. Profitability calculated by cash flow analysis. Production capacity: 30–37 kt/y butadiene.	Deterministic. Cradle to gate. GWP, CED, and 10 more impacts. GWP compared to naphtha-cracking route. LCA modelling with SimaPro software.	Very low probability to be profitable. Significant GHG reduction compared to naphtha-derived butadiene.
Moncada et al. (2018)	One-step	Azeotropic ethanol from C6 sugars	Netherlands	Catalyst performance data from experts. Process modelling in Aspen Plus. Biorefinery co-producing butadiene and caprolactam with common CHP system. Byproducts are sold.	Deterministic. Profitability calculated by cash flow analysis. Production capacity: 24 kt/y butadiene.	Not performed.	Butadiene production from C6 sugars is not profitable for average market prices.
Cabrera Camacho et al. (2020)	One-step	Azeotropic first-generation ethanol from regional crops	US, Europe, Brazil	Catalyst performance model developed from catalytic tests by authors to account for impurities in ethanol. Process modelling in Aspen Plus. Two scenarios: (i) low and (ii) high catalyst selectivity. Stand-alone plant. Byproducts are sold.	Deterministic. Cost calculations for a generic location based on international prices. Profitability calculated by cash flow analysis. Production capacity: 200 kt/y butadiene.	Stochastic. Cradle to gate. GWP, WC, and CED impacts. Comparison with naphtha-cracking route. LCA modelling with SimaPro software, ecoinvent database, and literature survey.	Ethanol-derived butadiene is not profitable for average market prices. Brazil is the best location in terms of GWP and WC, and the only one with GWP reduction relative to naphtha-derived butadiene.
Dimian et al. (2021)	Two-step	Azeotropic ethanol. Feedstock for ethanol production unknown.	–	Catalyst kinetic models from literature for first and second step. Process modelling in Aspen Plus. Stand-alone plant. Alternative separation train. Byproducts are sold.	Deterministic. Profitability calculated by cash flow analysis. Production capacity: 91 kt/y butadiene.	Not performed	Ethanol-derived butadiene is profitable for average market prices.
Rodgers et al. (2022)	One-step	Ethanol from syngas (supercritical water gasification of woody biomass or black liquor)	China	Catalyst performance data for second step taken from the literature. Process modelling in Aspen Hysys. Two routes for ethanol: (i) fermentation of syngas from black liquor and (ii) catalytic conversion of syngas from woody biomass. Common CHP system for ethanol and butadiene production. Byproducts are sold.	Stochastic. Profitability calculated by cash flow analysis. Production capacity: 9–31 kt/y butadiene.	Deterministic. Cradle to gate. Only GWP impact. Comparison with naphtha-cracking route. LCA modelling with SimaPro software.	Only syngas fermentation route can be profitable but with low probability. Both routes with GWP reduction relative to naphtha-derived butadiene.
This work	One- and two-step	Azeotropic first-generation ethanol from sugarcane	Brazil	Catalyst performance from catalytic tests by authors where impurities in ethanol are accounted for. Process modelling in Aspen Plus. Two scenarios for each route: (i) low and (ii) high catalyst selectivity. Stand-alone plant. Byproducts are sold.	Stochastic. Cost calculations for Brazil. Profitability calculated by cash flow analysis. Production capacity: 200 kt/y butadiene.	Stochastic. Cradle to gate. GWP, WC, and CED impacts. Comparison with naphtha-cracking route. LCA modelling with SimaPro software, ecoinvent database, and literature survey.	One-step process has higher probability than two-step process to be profitable. Expected environmental impact of two-step process is higher than one-step process in all impact categories.
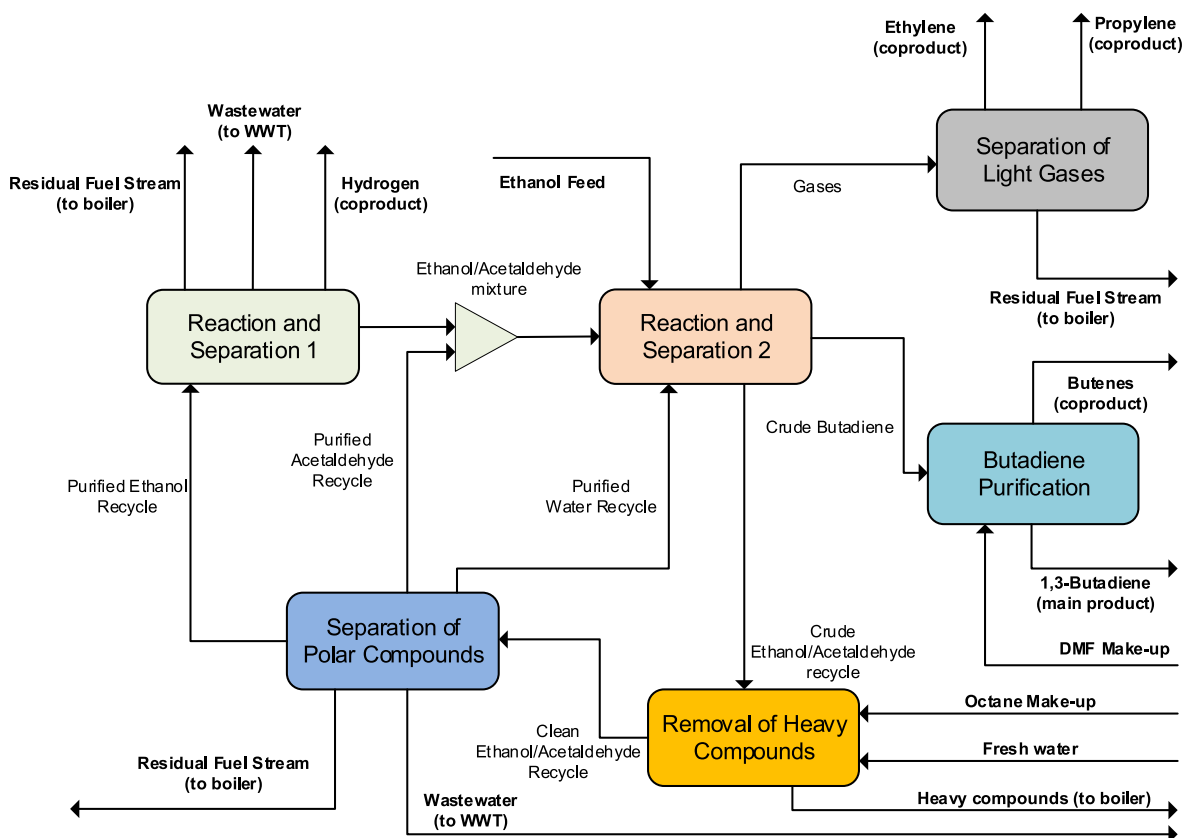
Fig. 1. Block diagram of the two-step process.

acetaldehyde content and a crude ethanol/acetaldehyde mixture (reaction and separation 2, Fig. 1).

In the purification train of 1,3-BD, crude butadiene is scrubbed with water (purified water recycle to reaction and separation 2, Fig. 1) to remove acetaldehyde, and then butenes are separated by extractive distillation with dimethylformamide (DMF), resulting in highly pure 1,3-BD (99.9 wt%; butadiene purification, Fig. 1). The crude ethanol/acetaldehyde mixture contains heavy compounds that must first be removed because otherwise they would hinder the later recovery of ethanol and acetaldehyde by distillation (Dastillung et al., 2016). These heavy compounds are extracted using an organic solvent (removal of heavy compounds, Fig. 1). The removed heavy compounds are burnt in the plant as fuel, while the clean acetaldehyde/ethanol mixture is sent to a train of distillation columns where water and remaining byproducts are removed from acetaldehyde and ethanol (separation of polar compounds, Fig. 1). Several streams result from all these separations: i) a stream of purified ethanol (7.5 wt% water), a fraction of which is fed to the first reactor and the rest used as solvent in the scrubbers; ii) a purified acetaldehyde stream that is fed to the second furnace reactor; iii) a mixture of minor byproducts that is burnt in the plant as fuel (residual fuel stream); iv) a purified water stream that is recycled and used as a mass separation agent; and v) a water stream polluted with organic byproducts that is treated in a Fenton process (WWT; Iboukhoulef et al., 2016).

A stream from the separation train after the second reactor comprises propylene and ethylene (gases) that are separated (separation of light gases, Fig. 1). Recovered ethylene, propylene, and butenes are sold as coproducts.

2.2. Modelling of the two-step process

The modelling of the two-step process was carried out with Aspen Plus V8.8. For the simulation of each section of the plant, suitable

thermodynamic methods were selected. The SRK equation of state was chosen for the separation of ethylene and propylene (separation of light gases), the Wilson method for extractive distillation with DMF in the butadiene separation section, and the NRTL method for simulation of the rest of the plant. Validation and calibration of these thermodynamic models were carried out in a previous work (Cabrera Camacho et al., 2020). Rigorous models in Aspen Plus based on equilibrium stages (RadFrac and Extract models) were used to simulate separation process units such as distillation columns, absorbers, and extraction columns.

For modelling the dehydrogenation reactor, experimental data from ethanol dehydrogenation (Eq. (1)) over a conventional Cu/SiO₂ catalyst (Klein et al., 2016) were used to estimate the reaction conditions for a target ethanol conversion (footnote g, Table 2), so the mixing of the acetaldehyde and ethanol from the first reactor and the acetaldehyde recycled to the second reactor resulted in the desired ethanol/acetaldehyde ratio in the feed to the second reactor. The dehydrogenation reactor was modelled in Aspen Plus as a stochiometric reactor (RStoic model) considering only the ethanol dehydrogenation reaction (Eq. (1)) since no side reactions were observed based on the experimental data (Klein et al., 2016).

The catalytic reactor for the second reaction step was modelled in Aspen Plus as a yield reactor (RYield model) based on the experimental per-pass conversion of acetaldehyde and ethanol and carbon selectivity to products for the two selected catalysts. In scenario B3, the performance data of a Ta/SBA-15 catalyst from experiments conducted in our laboratory with aqueous ethanol/acetaldehyde mixtures as feed were employed (Cabello González et al., 2022). When choosing the reaction conditions for this catalyst (space velocity, reaction temperature, ethanol/acetaldehyde mole ratio, and water mass content in the reactor feed), two design decisions were made: (i) the water content in the acetaldehyde/ethanol mixture should be 7.5 wt% to avoid the costly separation of the water-ethanol azeotrope (Cabrera Camacho et al., 2020) and (ii) the ethanol/acetaldehyde mole ratio should be low

Table 2

Catalyst operating conditions and performance for each scenario.

Process	One-step		Two-step	
Scenario	B1[f]	B2[f]	B3[g]	B4[g]
Catalyst	Hf–Zn	Hf–Zn	Ta-SBA-15	TaSiBEA
Operating conditions				
Temperature (°C)	380	360	350	350
Water in reactor feed (wt%)	7.5	7.5	7.5	7.5[h]
WHSV[a] (1/h)	1.12	0.64	1.63	0.79
Ethanol conversion (%)	81.9	87.1	49.3	38.6[b]
Acetaldehyde conversion (%)	–	–	70.8	52.4[b]
Ethanol/acetaldehyde (mole ratio)	–	–	1.7	2.2
Carbon selectivity (%)				
Ethylene	9.9	14.6	3.2	3.0
Propylene	2.9	3.3	2.0	1.0
1-butene	2.7	2.1	1.5	2.0[e]
1,3-BD	58.8	69.5	77.4	87.5
2-trans-butene	2.7	2.1	1.5	2.0[e]
Acetaldehyde	8.1	4.1	–	–
Diethyl ether	1.3	2.6	2.5	1.0[e]
Acetone	1.4	0.5	2.4[d]	1.0[e]
N-butanol	0.2	0.1	–	–
N-butanal	3.6	1.1	3.6[d]	1.0[e]
Heavy compounds	8.4	0.0	5.9[c]	1.5[c,e]
1,3-BD carbon yield (%)	48.2	60.5	44.3	37.5

[a] Weight hourly space velocity (WHSV, 1/h) is defined as the ratio of mass flow of acetaldehyde and/or ethanol (kg/h)/load of catalyst (kg).

[b] Personal communication with Dr. Kyriienko (June 15, 2019).

[c] Heavy compounds modelled as diethoxyethane.

[d] Numerous oxygenated compounds observed in the experiments are lumped into n-butanal and acetone.

[e] The "others" fraction reported by Kyriienko et al. (2016) was assumed to be a mixture of butenes and diethyl ether, while the crotonaldehyde fraction was assumed to be a mixture of oxygenated compounds (acetone and n-butanal) and heavy compounds.

[f] From Cabrera Camacho et al. (2020)

[g] Estimated operation conditions of the dehydrogenation reactor are T = 225 °C, P = 1.5 bar, and WSHV~0.237 1/h for a target ethanol conversion of 44.4% and 42.1% for B3 and B4 scenarios, respectively.

[h] It is assumed that catalyst performance is not affected by water at 350 °C, as observed for the Ta-SBA-15 catalyst.

enough to avoid a large ethanol recycle stream in the process but high enough to achieve a high selectivity to 1,3-BD in the second reaction step. In Table 2, the selected operating conditions are shown for which the highest experimental selectivity to 1,3-BD was obtained (~77%) at a low ethanol/acetaldehyde mole ratio (1.7 compared to 2.7 for the industrial process; Kyriienko et al., 2016). In scenario B4, the impact of using a catalyst more selective to 1,3-BD on the performance of the process was examined. One of the most selective two-step catalysts reported in the literature, a TaSiBEA zeolite (Kyriienko et al., 2016), was selected (Table 2) that exhibits higher 1,3-BD selectivity than the Ta-SBA-15 catalyst (~87% compared to ~77%) but at the expense of a higher ethanol/acetaldehyde mole ratio (2.2 compared to 1.7).

For the sake of later comparison between the one- and two-step processes, the performance of the catalysts considered in the one-step process scenarios (B1 and B2) are shown in Table 2.

As in our previous study on the one-step process, the process plant was heat integrated. The heat exchanger network (HEN) was optimally designed using the tool Aspen Energy Analysis, which considers the capital and operating costs associated to the HEN. Appropriate heating and cooling utilities were chosen to satisfy the energy demand of the plant at different temperature levels. In the furnace reactors, natural gas was burnt to provide heat. In the Supporting Information section (Appendix C), more details are provided on the heat integration and resulting HEN of the two-step process.

2.3. Economic assessment

The methodology for the economic calculations is described in our

previous work on the one-step process (Cabrera Camacho et al., 2020), and for the sake of the reader is presented again in Appendix A. The minimum butadiene selling price (MBSP, €/t) was chosen as an economic indicator for comparing the economics of each scenario, and it is defined as the selling price of 1,3-butadiene to recover the capital investment with a 10% rate of return at the end of the plant life. The MBSP was calculated from a cash flow analysis based on the economic assumptions shown in Table A4. The capital expenditures (CAPEX; Table A1), operating expenditures (OPEX; Table A2), and revenue from byproducts (Table A3) were calculated using economic information for Brazil as the plant location whenever possible. A sensitivity analysis was performed using a tornado chart to determine what economic parameters had the largest influence on the MBSP for each scenario. These economic parameters were the price of ethanol and the cost of natural gas. An uncertainty analysis using the Monte Carlo method implemented in a self-made cost spreadsheet was performed by simultaneously sampling the market price of bioethanol, natural gas, and butadiene from historical data to determine the probability of each scenario being profitable (net present value [NPV] > 0). For that purpose, historical data of the market price of azeotropic sugarcane bioethanol (CEPEA, 2022) and industrial natural gas (Agência Nacional do Petróleo, n.d.; COGEN.com, n.d.) in Brazil as well as the international market price of butadiene (IHS Markit, 2019; Rodgers et al., 2022) were used. These historical data are shown in Appendix D. The Monte Carlo simulation was run 9000 times for each scenario to ensure a certain statistical accuracy in the estimation of the NPV distribution (Appendix D).

2.4. Lifecycle assessment

The 100-year global warming potential (GWP), water consumption (WC), and cumulative energy demand (CED) were assessed in the present paper for 1,3-BD production from sugarcane bioethanol in Brazil via the two-step process (scenarios B3 and B4) and compared with those environmental impacts previously obtained for the one-step process in Brazil (scenarios B1 and B2) and the naphtha-cracking process (Cabrera Camacho et al., 2020). The GWP and WC impact categories were selected because fighting climate warming is one of the main goals when adopting bio-based industries, and water is a valuable and scarce natural resource. The CED impact category was selected because it is a useful indicator of the overall environmental impact of a product (Huijbregts et al., 2006).

Although the methodology for the LCA was thoroughly described in our previous study on the one-step process (Cabrera Camacho et al., 2020), a summary is provided for the sake of the reader. Following the guidelines of the ISO 14040/44 standards (ISO, 2006a, 2006b), an attributional LCA was performed using SimaPro software version 8.5.2.0 (Pré Consultants, 2017), the Ecoinvent (V3) database (Ecoinvent Centre, 2018), the ReCiPe 2016 midpoint characterization method (V 1.02), and the CED method (V 1.10) for lifecycle modelling, background data for inventory, environmental impact, and CED calculation. One t of produced 1,3-BD was chosen as the functional unit. A cradle-to-gate approach was applied. Background inventory data from the Ecoinvent (V3) database (Ecoinvent Centre, 2018) were used for those consumables and utilities needed in the 1,3-BD production process, including the ethanol supply chain. Foreground inventory data were sourced from the energy and mass balances from the simulations (reported in Cabrera Camacho et al., 2020, for cases B1 and B2 and in Table A7 of this manuscript for scenarios B3 and B4). In the case of the GWP, the end of life of 1,3-BD was considered (Institute of Scrap Recycling Industries [ISRI], 2009) as suggested by Shylesh et al. (2016). The background data to produce 1,3-BD from naphtha were taken from the Ecoinvent V3 database (Ecoinvent Centre, 2018).

3. Results and discussion

3.1. Overall mass and energy balances

The overall mass and energy balances of B3 and B4 scenarios along with those of B1 and B2 are shown in Table 3 for comparison. Process stream tables for scenarios B3 and B4 can be found in Appendix B. As expected, the overall 1,3-BD productivity (B1 = 0.334; B2 = 0.400; B3 = 0.443; B4 = 0.508 t 1,3-BD/t anhydrous ethanol) increases with catalyst selectivity to 1,3-BD. A larger 1,3-BD productivity means a lower amount of raw ethanol and a lower generation of valuable byproducts such as ethylene, propylene, and butenes. A decrease in the generation of residual fuel streams (comprised by light oxygenates and heavy compounds) from scenario B1 to B4 would also be expected, but it increases from scenario B2 to B3 because of the greater aggregate selectivity to light oxygenates and heavy compounds of scenario B3 (14.4%) compared to scenario B2 (8.4%; Table 2). Although the generation of these residual fuel streams is unwanted, they help reduce the heating utility consumption of the process by burning them in a steam boiler.

The energy balances show that the total consumption of heating and cooling utilities of the two-step process scenarios is higher than that of the one-step process scenarios (B1 = 29.1; B2 = 25.5; B3 = 51.7; B4 = 59.3 GJ/t 1,3-BD). The main reason for this is the operation with a large excess of ethanol in the second reaction step of the two-step process, which entails a larger consumption of natural gas in the furnace reactors and greater heating (MPS and LPS) and cooling water demands in the separation train to recover and recycle ethanol. These effects prevail over the reduction in natural gas consumption of the furnace reactors and utility demand of the separation train due to the lower quantity of raw ethanol to be processed and byproducts to be separated, respectively. The greater 1,3-BD productivity of the two-step processes is at the expense of higher energy consumption than the one-step processes. For two-step processes, a higher overall 1,3-BD productivity might imply a larger total energy-specific consumption, as observed by comparing scenarios B3 and B4 (Table 3). The larger 1,3-BD selectivity of scenario B4 is achieved at the expense of operating at a larger ethanol/

acetaldehyde ratio than scenario B3. In scenarios B3 to B4, the opposing effects of 1,3-BD selectivity and the ethanol/acetaldehyde ratio on utility consumption counterbalance each other, and the lower energy consumption of scenario B3 with respect to scenario B4 is explained by the larger amount of steam generated from the energetic valorization of the residual fuel streams.

To summarize, the overall 1,3-BD productivity of two-step processes is larger than that of one-step processes due to the higher 1,3-B selectivity of two-step catalysts, resulting in an important reduction in ethanol consumption. This higher productivity is at the cost of operating with large ethanol recycles, which dramatically increases specific energy consumption. The difference in ethanol and energy consumption will significantly determine the relative economic and environmental performance of the processes, as shown in Sections 3.2 and 3.3.

A comparison of the overall mass and energy balances of published works on ETB processes is shown in Table 4. The productivity of 1,3-BD reflects the mass conversion efficiency of ethanol into butadiene, while the total utility consumption indicates how much thermal energy must be put into play. The conclusion reached in the present study that the specific energy demand is larger for two-step processes than one-step processes cannot be deduced from the published works. The main reason for this is the disparity in the decisions made in those works regarding heat integration. In some works, byproducts are combusted in the CHP system of the process, and/or the process is heat integrated with an adjacent ethanol plant. Both decisions decrease the utility demand, so a comparison with works in which those decisions are not made is not fair; indeed, opposing results are obtained. For instance, Moncada et al. (2018) and Cespi et al. (2016) reported one- and two-step processes, respectively, with close 1,3-BD productivity in which the specific utility demand of the two-step process is lower, while just the opposite occurs when comparing the one- and two-step processes reported by Cespi et al. (2016) and Dimian et al. (2021), respectively.

3.2. Economic assessment

Fig. 2 depicts a breakdown of the MBSP for all scenarios (OPEX and CAPEX are shown in Table A5). The MBSPs of the one-step process

Table 3
Results of the overall mass and energy balances for the one- and two-step process scenarios.

Scenarios			B1	B2	B3	B4
Item		Unit	unit/t BD	unit/t BD	unit/t BD	unit/t BD
Inputs	**Total**	t	3.800	3.125	2.462	2.137
Raw material	Ethanol (93 wt%)	t	3.220	2.690	2.425	2.116
solvents	Octane	t	0.003	0.001	0.036	0.020
	Water	t	0.575	0.432	0.000	0.000
	DMF	t	0.001	0.001	0.001	0.001
Outputs	**Total**	t	3.800	3.125	2.461	2.136
Products	1,3-BD	t	1.000	1.000	1.000	1.000
	Butenes	t	0.097	0.062	0.040	0.048
	Ethylene	t	0.155	0.197	0.035	0.029
	Propylene	t	0.054	0.049	0.015	0.003
	Acetaldehyde	t	0.127	0.000	0.000	0.000
	Hydrogen	t	0.047	0.042	0.040	0.029
To boiler	Residual fuel streams	t	0.460	0.235	0.381	0.139
To treatment	Wastewater	t	1.861	1.539	0.950	0.888
Utility Demand[a]	**Total**	GJ	29.109	25.483	51.729	59.347
Heating	Total	GJ	9.416	10.781	21.585	28.177
	HPS	GJ	0.025	3.326	4.106	4.100
	MPS	GJ	0.225	0.093	0.787	0.753
	LPS	GJ	1.325	0.775	5.094	11.644
	Natural gas	GJ	7.841	6.588	11.598	11.680
Cooling	Total	GJ	19.693	14.702	30.144	31.170
	Cooling water	GJ	15.926	11.323	28.845	28.478
	Chilled water	GJ	0.227	0.000	0.008	0.107
	Refrigerant 1	GJ	3.347	3.194	1.291	2.585
	Refrigerant 2	GJ	0.193	0.186	0.000	0.000
Electricity		kWh	500.7	344.6	656.6	564.8

[a] Properties and temperatures of each utility are provided in Table C1. Total utility demand excludes electricity.

Table 4
Summary of overall mass and energy balances of published works on ETB processes.

Process	Work	Scenario	Productivity (t BD/t ethanol)	Total utility demand[g] (GJ/t BD)	Byproduct energy valorization[b]	Integration adjacent plant[c]
One-step	Cespi et al. (2016)	–	0.511	11.4	Yes	No
	Shylesh et al. (2016)	–	0.550	6.2[a]	No	Yes
	Moncada et al. (2018)[h]	Case I	0.279	11.5	No	Yes
		Case I	0.395	6.9	No	Yes
	Cabrera Camacho et al. (2020)	B1	0.334	29.1	No	No
		B2	0.400	25.5	No	No
	Rodgers et al. (2022)[e]	–	–	–	Yes	Yes
Two-step	Cespi et al. (2016)	–	0.281	8.8	Yes	No
	Farzad et al. (2017)[d]	BD-c	0.331	11	Yes	Yes
	Dimian et al. (2021)	–	0.495	15.8	No	No
	This work	B3	0.443	51.7	No	No
		B4	0.508	59.3	No	No

[a] Only consumption of heating utilities was reported.
[b] Byproducts are not sold but combusted to provide heat to the process.
[c] The ETB plant is heat integrated with an adjacent ethanol plant.
[d] Coal burning scenario (BD-c) in which coal is burnt in a CHP system to satisfy the energy deficit.
[e] Productivity and utility demand are not available because overall mass and energy balances were not reported.
[g] Sum of heating and cooling utility demand, electricity excluded.
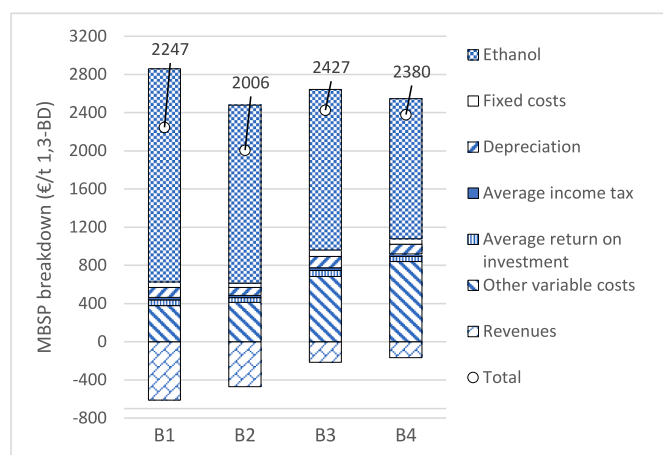[h] Case I is the base case, while in Case II better catalyst performance is assumed.

Fig. 2. Breakdown of minimum butadiene selling price for all scenarios. The figure over each bar is the net MBSP when byproduct revenues are accounted for. Numerical values can be found in Table A6.

scenarios are lower than those of the two-step processes, with the lowest MBSP for scenario B2 (2006 €/t). This is remarkable since the 1,3-BD productivity of the one-step process scenarios is lower. Fig. 2 shows that the MBSP is mostly determined by the OPEX since the impact of the CAPEX on the MBSP through return on investment and depreciation is relatively low (5.7, 5.3, 6.9, and 6.2% of the MBSP from B1 to B4 scenarios). Ethanol accounts for the highest operating cost (78.1, 75.3, 63.6, and 57.6% of the MBSP from B1 to B4 scenarios), followed by energy costs (utilities and natural gas; 7.1, 10.6, 16.9, and 23.8% of the MBSP from B1 to B4 scenarios). The larger 1,3-BD productivity of the two-step scenarios means lower ethanol costs than with one-step scenarios, but this cost reduction is more than offset by the larger energy costs, resulting in higher MBSP than one-step process scenarios. The MBSP of the two-step scenarios are almost equal. The reduction in ethanol cost for the higher productivity of the B4 scenario is almost counterbalanced by the increase in energy costs because of operating at a larger ethanol/acetaldehyde mole ratio than the B3 scenario. In one-step process scenarios, the larger ethanol costs are compensated by a lower energy cost and higher revenues from byproducts, the latter a consequence of the lower selectivity to 1,3-BD, resulting in lower MBSP than the two-step scenarios. For the design capacity chosen in this work (200 kt 1,3-BD/y), the CAPEX fluctuates from 0.9 to 1.1 M€/kt 1,3-BD

for one-step processes and 1.0–1.4 M€/kt 1,3-BD for two-step processes.

A sensitivity analysis of the MBSP of each scenario was performed by changing ±20% the nominal values of the economic parameters that have the largest influence on the MBSP: CAPEX and the market price of ethanol, natural gas, and byproducts (Fig. 3). As expected, the sensitivity of the MBSP to the price of ethanol is substantial, and it is larger for one-step process scenarios since the production of 1 t of 1,3-BD requires a greater amount of ethanol, while greater sensitivity to the natural gas price in two-step process scenarios is explained by their greater specific energy consumption (the natural gas price influences the costs of heating and cooling utilities according to the correlations used for their estimation; Table A2). The sensitivity of MBSP to the prices of byproducts, assuming a simultaneous change in all of them, is important only for one-step process scenarios. Changes in CAPEX have the smallest impact on the MSBP for all scenarios.

The nominal MBSP of all scenarios (Fig. 2) is greater than the average international market price of 1,3-BD in the last decade (1423 €/t; IHS Markit, 2019; Rodgers et al., 2022), so the scenarios are not expected to be profitable. Since the economics of one- and two-step process scenarios is highly dependent on the prices of ethanol and natural gas, and they vary over time, an uncertainty analysis was performed as explained in Section 2.3 to evaluate the probability that the scenarios are profitable. The results show (Fig. 4) that the probability that any scenario is profitable (NPV >0) is low (B1: 11.1%, B2: 17%, B3:5.5%, and B4: 5.5%). The one-step process scenarios have a higher probability of being profitable, with the highest probability for scenario B2.

The MBSPs reported on previous TEAs on ETB processes are shown in Table 5. All MBSPs except one (case Acet-BD; Rodgers et al., 2022) are greater than the average market price of butadiene in the last decade, so the ETB route, either by one- or two-step reaction, is not expected to be profitable. This was confirmed by works (Table 5, last column) in which uncertainty analyses were performed by varying the most influencing economic parameters based on historical data. The uncertainty analyses revealed that the probability of being profitable for one-step processes, although low, is higher than that of two-step processes.

3.3. Lifecycle assessment

In this section, three environmental impacts (GWP100, WC, and CED) of the production of 1,3-BD from sugarcane bioethanol (scenarios B1 to B4) in Brazil are compared to those of the naphtha steam-cracking route.

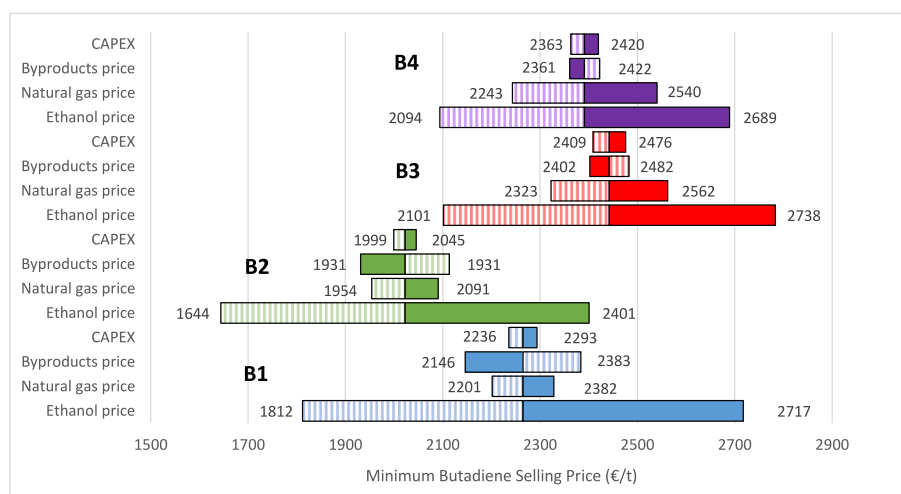Because ethanol is the main contributor to the three analyzed impact

Fig. 3. Sensitivity of MBSP of each scenario to CAPEX and the market prices of ethanol, natural gas, and byproducts. Solid bar: +20% change. Striped bar: −20% change.
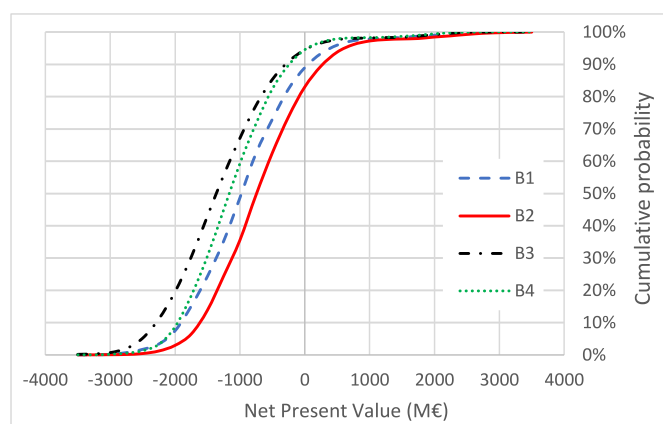

Fig. 4. Results of economic uncertainty analysis. Probability of achieving a NPV lower than a numerical value when considering simultaneous variations in the market price of bioethanol, natural gas, and butadiene based on historical data.

categories, a calculation of uncertainties in the impact factors related to the background inventory data for ethanol production from sugarcane in Brazil was considered based on the literature review undertaken by the authors (Cabrera Camacho et al., 2020). For each impact category, the scores obtained by using background data from the Ecoinvent (V3) database are discussed first, followed by the uncertainty analysis results.

3.3.1. Global warming potential

The score of this impact category is shown for each scenario in Fig. 5. B2 is the scenario with the lowest GWP100 score, followed by the B3, B1, and B4 scenarios, with 111, 143, 152, and 160% higher score than that of the naphtha-based production of 1,3-BD. The GWP100 scores of the scenarios would be even higher if the end of life of 1,3-BD were not considered.

Ethanol production is the main contributor to GWP100, accounting for 84% (B1), 81% (B2), 70% (B3), and 59% (B4) of the total impact in each scenario. The contribution of ethanol to GWP100 decreases with catalyst selectivity to 1,3-BD as lower raw ethanol is consumed, but fewer credits from byproduct substitution are obtained. Most of these credits come from hydrogen (53–60% for one-step scenarios and 80–82% for two-step scenarios) and ethylene (15–25% for one-step scenarios and 6–7% for two-step scenarios). As 1,3-BD catalyst

Table 5
Summary of TEA studies on ETB processes.

Process	Work	Scenario	Production Capacity (kt/y)	Required IRR (%)	MBSP (€/t)[a]	Uncertainty analysis[e]
One-step	Moncada et al. (2018)[b]	Case I	24	10	4980	No
		Case II	34	10	3883	No
	This work	B1	200	10	2247	Yes (11.1%)
		B2	200	10	2006	Yes (17%)
	Rodgers et al. (2022)[d]	Acet-BD	9	10	1367	Yes (19%)
		Eth-BD	36	10	1954	Yes (1%)
Two-step	Farzad et al. (2017)[c]	BD-b	30	10	3068	Yes (0%)
		BD-c	37	10	2766	Yes (0%)
	Dimian et al. (2021)	–	91	ROI = 13%	1660	No
	This work	B3	200	10	2427	Yes (5.5%)
		B4	200	10	2380	Yes (5.5%)

[a] Prices have been adjusted for inflation to 2022 (multiplication by 1.16, 1.14, and 1.09 of the reported MBSPs; Farzad et al., 2017; Moncada et al., 2018; Dimian et al., 2021).

[b] Case I is the base case, while in Case II, better catalyst performance is assumed.

[c] Bd-b is a self-sufficient energy scenario in which a fraction of biomass feed is burnt in the CHP system to satisfy the energy deficit of the process, while in the BD-c scenario, imported coal is burnt instead.

[d] In the Acet-BD scenario, black liquor is gasified, syngas fermented to acetaldehyde, then hydrogenated to ethanol, which is converted to butadiene. In the Eth-BD scenario, pulpwood is gasified, syngas converted into mixed alcohols, and separated ethanol converted into butadiene.

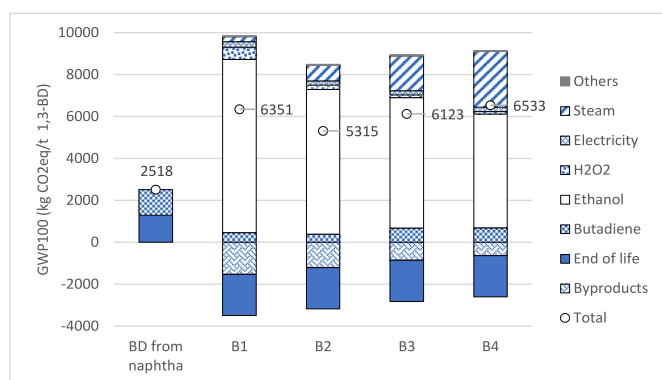[e] Numbers shown in brackets is the probability of NPV>0.

Fig. 5. GWP100 scores for each scenario considering Brazil as the plant location and the end of life of 1,3-BD as styrene-butadiene rubber for automotive tires (Shylesh et al., 2016). CO_2 emissions from burning natural gas are accounted for as direct process emissions (butadiene category). The data for background inventory were taken from Ecoinvent (V3) database. "Others" comprises solvents, catalysts, adsorbents, and disposal of residues.

selectivity increases from scenario B1 to B4, the decrease in ethanol impact on GWP100 outweighs the loss of credits by the reduced production of byproducts. For the two-step process scenarios, the benefits of high 1,3-BD selectivity are exceeded by the negative impact of the high energy (steam and natural gas) consumption, resulting in larger GWP100 scores than the best one-step process scenario (B2).

The range of expected GWP100 scores for each scenario due to uncertainty in the impact value of Brazilian sugarcane-based ethanol is shown in Fig. 6. The median GWP100 scores from the uncertainty analysis are much lower than the scores shown in Fig. 5, the reason being that in the Ecoinvent V3 database, the contribution of the land-use change on the GWP impact value of Brazilian ethanol is quite large, resulting in an impact value five times the median value found in the literature (Cabrera Camacho et al., 2020). Only for the one-step process scenarios is a reduction in emissions of CO_2 almost certain with respect to the naphtha-cracking route since the whole interval of expected GWP100 scores for scenarios B1 and B2 is lower than the GWP100 score of the fossil route. Net carbon sequestration for the one-step process scenarios is very likely since the median value of their GWP100 score is negative (-73 and -52 kg CO_2eq/t 1,3-BD for B1 and B2 scenarios,

respectively). Based on CO_2 emissions, one-step processes should be preferred over two-step processes, whose environmental impact is worsened by CO_2 emissions related to the high consumption of fossil-derived utilities.

A comparison of our results on CO_2 emissions with other published works is difficult due to the differences in process design, assessment methodology, assumptions, and sources for background inventory, as discussed in the introduction section. A common conclusion of all LCA studies is that the main contributor to CO_2 emissions is the ethanol supply chain. From Table 6, it can be deduced that (i) the ETB route can achieve substantial reduction in CO_2 emissions related to the naphtha-cracking route and (ii) the use of second-generation ethanol results in lower CO_2 emissions than first-generation ethanol. Only with Brazilian sugarcane can ethanol CO_2 emissions be as low as those with second-generation ethanol. Since the second-generation ethanol industry is not yet well developed, Brazil is a suitable location for production of 1,3-BD from ethanol at industrial scale when considering ethanol availability and CO_2 emissions.

3.3.2. Water consumption

All bio-scenarios (B1 to B4) show much greater scores than the naphtha-based process (Fig. 7), mainly due to the irrigation water used in the cultivation of sugarcane for ethanol production, which ranges from 96 to 98% of the total WC for B1 and B2 scenarios and 95–97% for B3 and B4 scenarios. In this category, lower ethanol consumption per t of 1,3-BD is directly translated into a reduction in WC, resulting in 34% (B4), 25% (B3), and 18% (B2) reductions for these scenarios with respect to the highest score scenario (B1, with 964 m³/t 1,3-BD). Two-step processes are preferred over one-step processes in the WC category. This result is not in line with that of Cespi et al. (2016), who reported better WC scores for the one-step process than the two-step process owing to the lower 1,3-BD productivity they calculated for the two-step process (Table 6).

The uncertainty analysis (Fig. 8) shows a similar picture to single scores based on the Ecoinvent V3 database (Fig. 7), with lower median WC values for the two-step process scenarios, although the overlapping of the intervals of WC score between the different scenarios is significant. It can be concluded that it is likely that the two-step process can achieve a slightly better performance than the one-step process in terms of WC due to its lower ethanol consumption.

3.3.3. Cumulative energy demand

Fig. 9 shows that the CED of the 1,3-BD production from bioethanol is 202–258% greater than that from oil-derived naphtha. The supply chain of ethanol demands most of the energy (75–91%), and this percentage is larger for the one-step process scenarios due to their lower 1,3-BD productivity. The credits from byproducts, the second most important contribution for one-step process scenarios, help reduce the energy demand of those scenarios by ~12%, while for the two-step scenarios, the reduction is less significant (~6%). The non-renewable energy associated with the imported electricity, natural gas, and steam has a large impact on the two-step process scenarios (16 and 23% for B3 and B4, respectively), while it is not substantial in one-step process scenarios (5 and 8% for B1 and B2, respectively). Overall, the changes in the contributions of ethanol and utility consumption as well as byproducts when moving between scenarios cancel each other out, and the difference in the CED score among scenarios is low, except for scenario B1, with the largest CED score in which the ethanol impact is dominant due to the low 1,3-BD productivity. A common feature of all the scenarios is that most of the energy consumed is from renewable resources, in agreement with Cespi et al. (2016) and Farzad et al. (2017), and that the depletion of non-renewable resources is lower than producing 1,3-BD from oil-derived naphtha, particularly in one-step processes.

The uncertainty analysis shows that the median CED score for each scenario is close to its single CED score (Fig. 10) because the predicted
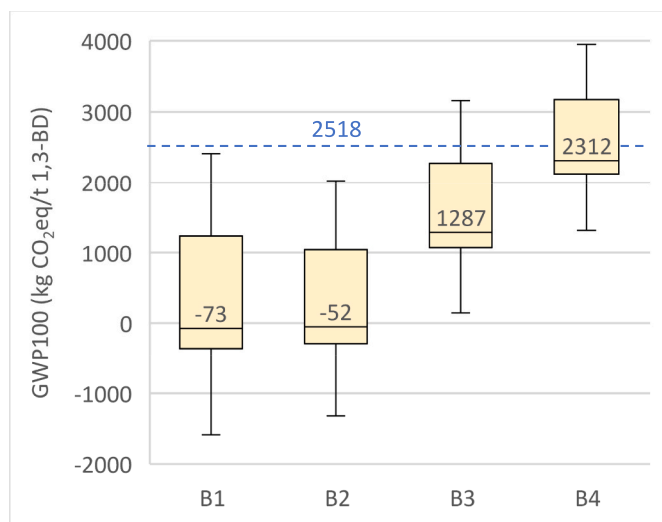

Fig. 6. Range of expected GWP100 scores for each scenario calculated using impact values of Brazilian sugarcane-based ethanol from the literature (Cabrera Camacho et al., 2020). The median score for each case is shown in each box. The CO_2 emission of the naphtha-cracking route is shown as a reference line.

Table 6
Summary of LCA studies on ETB processes.

Process	Work[b]	Scenario	Starting material[a]	Location	GWP (kg CO$_2$ eq/kg BD)[c]	CED (GJeq/t BD)[c]	WC (m^3/t BD)[c]
Naphtha-cracking	This work	–	Oil	Worlwide	2.5	65	7
One-step	Cespi et al. (2016)	–	SC	Brazil	1.04	82	19.95
		–	M	Europe	2.04	61	12.63
		–	CG	US	2.30	79	28.57
	Shylesh et al. (2016)	–	CG	US	1.82	–	–
		–	CS	US	−0.50	–	–
		–	SC	US	−0.60	–	–
	This work	B1	SC	Brazil	−0.07	251	299
		B2	SC	Brazil	−0.05	214	235
	Rodgers et al. (2022)	Acet-BD	BL	China	−3.23	–	–
		Eth-BD	PW	China	−2.80	–	–
Two-step	Cespi et al. (2016)	–	SC	Brazil	2.18	114	27.34
		–	M	Europe	3.62	84	16.81
		–	CG	US	4.00	110	39.73
	Farzad et al. (2017)	BD-b	B	South Africa	0.07	–	–
		BD-c	B	South Africa	0.06	–	–
	This work	B3	SC	Brazil	1.29	226	220
		B4	SC	Brazil	2.31	217	200

[a] B: bagasse; BL: black liquor; CG: corn grain; CS: corn stover; M: mixture of corn grain, wheat, rye, and sugar beet; PW: pulpwood; SC: sugarcane.

[b] All LCA studies are cradle-to-gate except Shylesh et al. (2016), and this work, which considers cradle-to-grave only for GWP.

[c] All reported values are from deterministic studies except for this work, in which median values from uncertainty analyses are used.
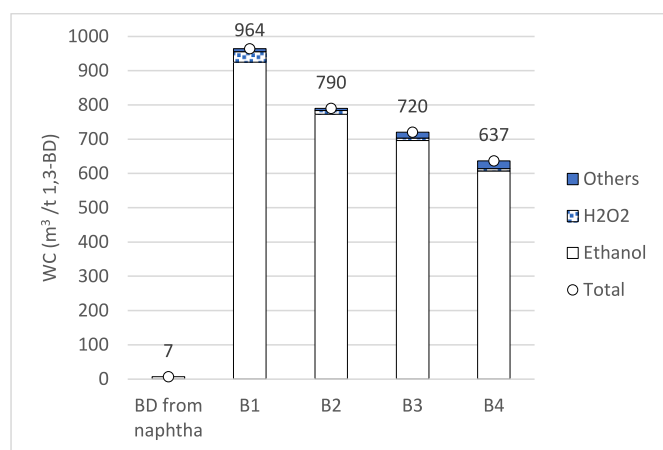

Fig. 7. Water consumption score for each scenario considering Brazil as the plant location. The data for background inventory were taken from the Ecoinvent (V3) database. "Others" comprises solvents, catalysts, adsorbents, and disposal of residues.

Fig. 8. Range of expected scores for WC calculated using the impact values of Brazilian sugarcane-based ethanol from the literature (Cabrera Camacho et al., 2020). The median score for each case is shown in each box. The WC of the naphtha-cracking route is shown as a reference line.

impact value for Brazilian sugarcane ethanol from the Ecoinvent database is very close to the median impact value from the literature (Cabrera Camacho et al., 2020). The high overlap between the CED intervals of the scenarios, except for B1, indicates that there is not a clear choice between one-step processes and two-step processes in the CED impact category. In the literature, only Cespi et al. (2016) compared the CED of one- and two-step processes (Table 6). They found that the CED score of the one-step process was lower, a consequence of the higher 1,3-BD productivity assumed in their work for the one-step process.

4. Conclusions

In the present work, the economic and environmental sustainability of 1,3-BD production from bioethanol through one and two reaction steps and the conventional naphtha-based route were compared. In the design and simulation of the one- and two-step process, experimental data of highly selective catalysts tested under simulated industrial operation conditions were used for a more rigorous assessment. Mass and energy balances for the economic assessment and the environmental performance of the one-step process were taken from a previous work by Cabrera Camacho et al. (2020), while the design and assessment of the
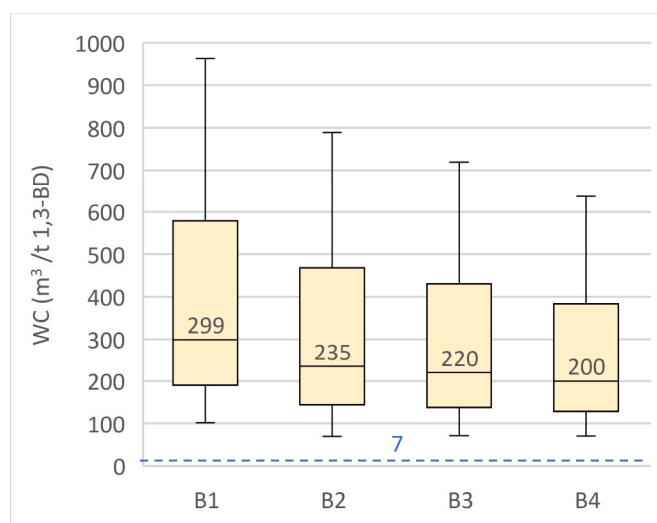
two-step process is fully addressed in the present work. Brazil was chosen as the plant location for the bioprocesses; the plant uses first-generation sugarcane ethanol as raw material (Cabrera Camacho et al., 2020). Stochastic analyses were carried out to assess the impact of uncertainty in the input data on the reliability of the economic and environmental results, which were compared with the literature.

The main appeal of two-step processes is their higher 1,3-BD selectivity, which results in ethanol consumption (1.96–2.25 t ethanol/t 1,3-BD) 10–35% lower than one-step processes (2.50–2.99 t ethanol/t 1,3-BD). Their higher 1,3-BD selectivity is achieved by operating with large ethanol recycles in the second reaction step, which considerably increases the specific energy consumption (52–59 GJ/t 1,3-BD) to around twice that of one-step processes (25–29 GJ/t 1,3-BD). The difference in the specific ethanol and energy consumption significantly determines the relative economic and environmental performance of the bioprocesses.

Bioethanol represents the dominant production cost. Two-step processes benefit from their lower ethanol consumption, but this is
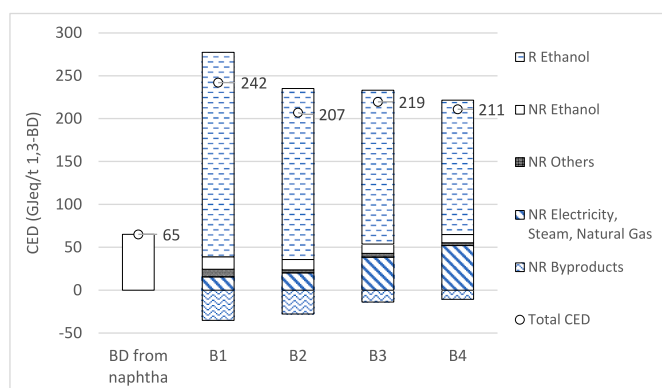
Fig. 9. Cumulative energy demand for each scenario broken down into non-renewable (NR) and renewable (R) energy. The data for background inventory were taken from the ecoinvent (V3) database. "Others" comprises solvents, catalysts, adsorbents, and disposal of residues.
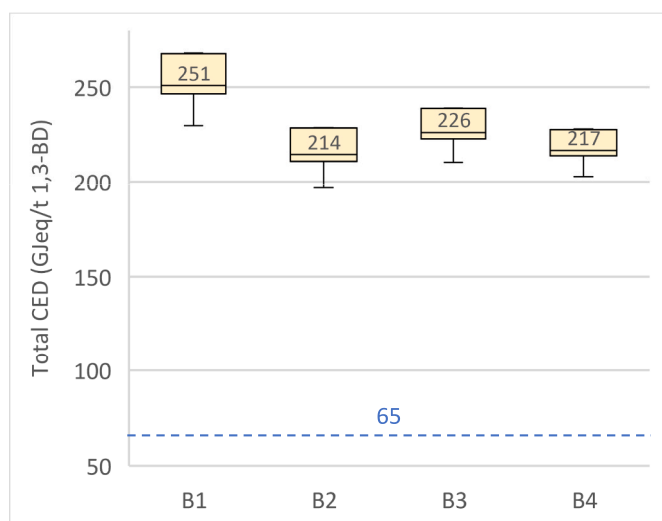

Fig. 10. Range of expected scores for cumulative energy demand calculated using the impact values of Brazilian sugarcane-based ethanol from the literature (Cabrera Camacho et al., 2020). The median score for each case is shown in each box. The cumulative energy demand of the naphtha-cracking route is shown as a reference line.

outweighed by their larger consumption of fossil-based utilities, resulting in greater production costs (2380–2427 €/t) than one-step processes (2006–2247 €/t). Uncertainty analyses based on the historical market prices of azeotropic ethanol and natural gas in Brazil, the most influencing economic parameters, show that 1,3-BD production from ethanol in Brazil is not expected to be profitable, with the probability of a positive NPV being 11–17% for one-step process scenarios and 5% for two-step process scenarios. This discourages investment in this conversion route even though producing butadiene from ethanol in Brazil can lead to significant reductions in emissions of CO_2 compared to naphtha-derived butadiene (from 7.6 to 103%), even leading to net carbon sequestration (from -0.05 to -0.07 kg CO_2eq/kg BD). A critical issue for the cost competitiveness of biobutadiene is that these CO_2 savings can be sold in an international carbon emission trading market. In that case, one-step processes, with much lower CO_2 emissions, would be much more favored than two-step processes. According to the literature (Table 6), the use of second-generation ethanol from lignocellulosic feedstock in 1,3-BD production also results in significant reduction in CO_2 emissions (from 97 to 230%), but second-generation ethanol is not widely available. Brazil is a suitable location for production of

renewable 1,3-BD from ethanol at industrial scale since sugarcane ethanol is highly available, and its use entails a large reduction in CO_2 emissions.

There are limitations in the present study. In the one- and two-step process scenarios, the plant was designed to be stand-alone and adjacent to a petrochemical complex. Heat and mass integration with the petrochemical complex, such as sharing existing purification units of the steam-cracking plant, could have improved the economic and environmental performance of the process scenarios. Only fossil-based utilities were considered in the study. The use of renewable fuels such as biomass residues to satisfy the heat demand of the processes could have resulted in lower production costs and CO_2 emissions.

These limitations open possibilities for future studies to follow up on the present work, for example integration of the ETB processes with petrochemical complexes and use of renewable utilities. Exergy and exergoeconomic evaluations of the ETB processes by which exergy losses and derived cost losses are detected would allow identifying design changes to improve the thermodynamic, economic, and environmental performance of the processes (Aghbashlo et al., 2018; Fallahi et al., 2021). Other future work could study the evolution of CO_2 markets and policies to determine the conditions under which ETB processes would be cost competitive if reductions in CO_2 emissions were credited.

Future research is needed regarding catalysis so that the two-step processes can compete with the one-step processes; this concerns the development of highly selective catalysts operating at low ethanol/acetaldehyde ratios for the second reaction step. This would reduce the energy demand of the two-step process and significantly improve its profitability and environmental sustainability.

CRediT authorship contribution statement

C.E. Cabrera Camacho: Investigation, Formal analysis, Software, Writing – original draft, Writing – review & editing. **A.L. Villanueva Perales:** Conceptualization, Formal analysis, Methodology, Supervision, Funding acquisition, Writing – original draft, Writing – review & editing. **Bernabé Alonso-Fariñas:** Methodology, Formal analysis, Writing – review & editing. **F. Vidal-Barrero:** Writing – review & editing, Funding acquisition. **Pedro Ollero:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2022.133963.

References

Agência Nacional do Petróleo, G.N. e B. Natural Gas Prices. n.d, (Publicidade dos Preços de Gás Natural) [WWW Document] Monthly Release of Natural Gas Trade, May 2022. (Boletim Mensal da Comercialização do Gás Natural, Mês de referência: Maio/2022). https://www.gov.br/anp/pt-br/assuntos/movimentacao-estocagem-e-com

ercializacao-de-gas-natural/acompanhamento-do-mercado-de-gas-natural/publicida de-dos-precos-de-gas-natural, 7.20.22.

Aghbashlo, M., Mandegari, M., Tabatabaei, M., Farzad, S., Mojarab Soufiyan, M., Görgens, J.F., 2018. Exergy analysis of a lignocellulosic-based biorefinery annexed to a sugarcane mill for simultaneous lactic acid and electricity production. Energy 149, 623–638. https://doi.org/10.1016/j.energy.2018.02.063.

Angelici, C., Weckhuysen, B.M., Bruijnincx, P.C.A., 2013. Chemocatalytic conversion of ethanol into butadiene and other bulk chemicals. ChemSusChem 6, 1595–1614. https://doi.org/10.1002/cssc.201300214.

Barnicki, S.D., Fair, J.R., 1990. Separation system synthesis: a knowledge-based approach .1. Liquid mixture separations. Ind. Eng. Chem. Res. 29, 421–432.

Barnicki, S.D., Fair, J.R., 1992. Separation system synthesis: a knowledge-based approach. 2. Gas/vapor mixtures. Ind. Eng. Chem. Res. 31, 1679–1694.

Cabello González, G.M., Concepción, P., Villanueva Perales, A.L., Martínez, A., Campoy, M., Vidal-Barrero, F., 2019. Ethanol conversion into 1,3-butadiene over a mixed Hf-Zn catalyst: effect of reaction conditions and water content in ethanol. Fuel Process. Technol. 193, 263–273. https://doi.org/10.1016/j.apcata.2018.11.010.

Cabello González, G.M., Villanueva Perales, A.L., Martínez, A., Campoy, M., Vidal-Barrero, F., 2022. Conversion of aqueous ethanol/acetaldehyde mixtures into 1,3-butadiene over a mesostructured Ta-SBA-15 catalyst: effect of reaction conditions and kinetic modelling. Fuel Process. Technol. 226 https://doi.org/10.1016/j.fuproc.2021.107092.

Cabrera Camacho, C.E., Alonso-Fariñas, B., Villanueva Perales, A.L., Vidal Barrero, F., Ollero, P., 2020. Techno-economic and life-cycle assessment of one-step production of 1,3-butadiene from bioethanol using reaction data under industrial operating conditions. ACS Sustain. Chem. Eng. 8, 10201–10211. https://doi.org/10.1021/acssuschemeng.0c02678.

CEPEA, 2022. Weekly index of hydrous ethanol for non-fuel use (indicador semanal do ethanol hidratado outros fins). CEPEA/ESALQ-Sao Paulo [WWW Document]. CEPEA - Centro de Estudos Avançados em Economia Aplicada. URL https://www.cepea.es alq.usp.br/br/indicador/etanol.aspx, 7.20.22.

Cespi, D., Passarini, F., Vassura, I., Cavani, F., 2016. Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. Green Chem. 18, 1625–1638. https://doi.org/10.1039/c5gc02148k.

COGEN.com. Releases of natural gas (Boletins de Gás natural). n.d, [WWW Document]. URL https://www.cogen.com.br/infocogen/documentos/boletins-de-gas-natural?Page=1, 7.20.22.

Consultants, Pré, 2017. SimaPro, PhD Version, 8.5.2.0.

Dastillung, R., Fischer, B., Jacquin, M., Huy-Ghe, R., 2016. Method for producing butadiene and hydrogen from ethanol in two low-water- and low-energy-consumption reaction steps (Procédé de production de butadiène et d'hydrogène à partir d'éthanol en deux étapes réactionnelles à faible consommation en eau et en énergie, WO2016042096A1.

Dimian, A.C., 2003. Chapter 7: process synthesis by hierarchical approach. In: Computer-Aided Chemical Engineering. Elsevier, pp. 229–298. https://doi.org/10.1016/S1570-7946(03)80031-7.

Dimian, A.C., Bezedea, N.I., Bildea, C.S., 2021. Novel two-stage process for manufacturing butadiene from ethanol. Ind. Eng. Chem. Res. 60, 8475–8492. https://doi.org/10.1021/acs.iecr.1c00958.

Ecoinvent Centre, 2018. Ecoinvent V3 Database.

Fallahi, A., Farzad, S., Mohtasebi, S.S., Mandegari, M., Görgens, J.F., Gupta, V.K., Lam, S.S., Tabatabaei, M., Aghbashlo, M., 2021. Sustainability assessment of sugarcane residues valorization to biobutadiene by exergy and exergoeconomic evaluation.

Renew. Sustain. Energy Rev. 147 https://doi.org/10.1016/j.rser.2021.111214, 111214.

Farzad, S., Mandegari, M.A., Görgens, J.F., 2017. Integrated techno-economic and environmental analysis of butadiene production from biomass. Bioresour. Technol. 239, 37–48. https://doi.org/10.1016/j.biortech.2017.04.130.

Huijbregts, M.A.J., Rombouts, L.J.A., Hellweg, S., Frischknecht, R., Hendriks, A.J., Van De Meent, D., Ragas, A.M.I., Reijnders, L., Struijs, J., 2006. Is cumulative fossil energy demand a useful indicator for the environmental performance of products? Environ. Sci. Technol. 40, 641–648. https://doi.org/10.1021/es051689g.

Iboukhoulef, H., Amrane, A., Kadi, H., 2016. Removal of phenolic compounds from olive mill wastewater by a Fenton-like system H2O2/Cu(II)—thermodynamic and kinetic modeling. Desalination Water Treat. 57, 1874–1879. https://doi.org/10.1080/19443994.2014.978385.

Institute of Scrap Recycling Industries (ISRI), 2009. Carbon Footprint of USA Rubber Tire Recycling 2007.

ISO, 2006a. Environmental management-life cycle assessment: principles and framework. Geneva-Switzerland.

ISO, 2006b. Environmental management-life cycle assessment: requirements and guidelines. Geneva-Switzerland.

Klein, A., Keisers, K., Palkovits, R., 2016. Formation of 1,3-butadiene from ethanol in a two-step process using modified zeolite-β catalysts. Appl. Catal. Gen. 514, 192–202. https://doi.org/10.1016/j.apcata.2016.01.026.

Kyriienko, P.I., Larina, O.v., Soloviev, S.O., Orlyk, S.M., Dzwigaj, S., 2016. High selectivity of TaSiBEA zeolite catalysts in 1,3-butadiene production from ethanol and acetaldehyde mixture. Catal. Commun. 77, 123–126. https://doi.org/10.1016/j.catcom.2016.01.023.

Moncada, J., Vural Gursel, I., Worrell, E., Ramírez, A., 2018. Production of 1,3-butadiene and ε-caprolactam from C6 sugars: techno-economic analysis. Biofuels, Bioprod. Biorefin. 6, 246–256. https://doi.org/10.1002/bbb.

Panahi, H.K.S., Dehhaghi, M., Kinder, J.E., Ezeji, T.C., 2019. A review on green liquid fuels for the transportation sector: a prospect of microbial solutions to climate change. Biofuel Res. J. 6, 995–1024. https://doi.org/10.18331/brj2019.6.3.2.

Pomalaza, G., Arango Ponton, P., Capron, M., Dumeignil, F., 2020. Ethanol-to-butadiene: the reaction and its catalysts. Catal. Sci. Technol. 10, 4860–4911. https://doi.org/10.1039/D0CY00784F.

Ren, T., Patel, M.K., Blok, K., 2008. Steam cracking and methane to olefins: energy use, CO2 emissions and production costs. Energy 33, 817–833. https://doi.org/10.1016/j.energy.2008.01.002.

Rodgers, S., Meng, F., Poulston, S., Conradie, A., McKechnie, J., 2022. Renewable butadiene: a case for hybrid processing via bio- and chemo-catalysis. J. Clean. Prod. 364 https://doi.org/10.1016/j.jclepro.2022.132614, 132614.

Shylesh, S., Gokhale, A.A., Scown, C.D., Kim, D., Ho, C.R., Bell, A.T., 2016. From sugars to wheels: the conversion of ethanol to 1,3-butadiene over metal-promoted magnesia-silicate catalysts. ChemSusChem 9, 1462–1472. https://doi.org/10.1002/cssc.201600195.

IHS Markit, 2019. Butadiene [WWW Document]. Chemical Economics Handbook. URL https://ihsmarkit.com/products/butadiene-chemical-economics-handbook.html (accessed 2.1.20).

Statista, 2017. Distribution of butadiene consumption worldwide as of 2017, by end use [WWW Document]. Chemicals & Resources-Chemical Industry. URL https://www.statista.com/statistics/725333/global-consumption-distribution-of-butadiene-by-end-use/ (accessed 8.16.18).