Techno-economic and life-cycle assessment of one-step production of 1,3-butadiene from bioethanol using reaction data under industrial operating conditions

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ABSTRACT

A process to produce 1,3-butadiene from ethanol in a one-step reaction with a Hf-Zn catalyst was designed using experimental data from the catalyst performance under industrial conditions, taking into account the presence of water and other by-products in recycled ethanol. The techno-economic and life cycle assessments of the process were performed and compared to the naphtha-cracking route. In these assessments two scenarios were defined to evaluate the impact of catalyst selectivity (58 and 69%). For the assessment of the environmental sustainability, three further cases were defined to determine the influence of the geographical location of the production plant considering the world's major ethanol suppliers: The United States, Brazil and Europe. The results of the economic evaluation show that for a plant with a production capacity of 200 ktonne/year of 1,3-BD, and considering an average market price of azeotropic ethanol (450 €/m3), the minimum butadiene selling price for a 10% rate of return on investment ranges 1.13-1.26 times the average butadiene market price (1529 €/tonne). The process can be profitable for favorable combinations of market prices of ethanol and 1,3-butadiene, but the profitability of the process ultimately relies on the development of higher selective catalysts to reduce the consumption of ethanol per tonne of 1,3-butadiene since ethanol dominates the production costs. The LCA shows that switching from naphtha-derived to bio-butadiene can lead to substantial reductions in CO2 emissions (GWP100) (8%-26%) but, in turn, to a significant increase in water consumption (62 to 137-fold) and cumulative energy demand (50-250%). Being that ethanol is the major contributor to all impact categories (65-98% of the impacts), the location of the plant and catalyst selectivity significantly affects the environmental sustainability of the process. Considering the three impact categories and the uncertainty analysis of the LCA results, the best plant location would be Brazil, with a negative median impact value for GWP100 (-73 to -52 kg CO_2eq/tonne 1,3-BD) and the lowest median value for blue water consumption (235-299 m^3/tonne 1,3-BD) but the highest median value for cumulative energy demand (207-241 GJeq/tonne 1,3-BD), the latter due to the low ethanol yield of sugarcane.

INTRODUCTION

Nowadays, 1,3-butadiene (1,3-BD) is an important building block for the production of synthetic rubbers and elastomers, such as styrene-butadiene-rubber (SBR), butadiene rubber (BR) and acrylonitrile-butadiene-styrene (ABS), among others[1–3]. Most 1,3-BD produced worldwide (95%) is obtained as a by-product of the manufacturing of ethylene by the steam cracking of naphtha, while the rest is by the catalytic oxidative dehydrogenation of n-butane and n-butene[4–6].

Within the context of searching for more sustainable development, the high energy demand and environmental burdens associated with the steam cracking of naphtha justify a renewed interest in the production of 1,3-BD from bioethanol, which is a largely- available and renewable resource. Some studies at an early stage of development[7,8] showed the potential economic and environmental advantages of 1,3-BD production from bioethanol over naphtha-based 1,3-BD.

The catalytic process for the production of 1,3-BD from ethanol at industrial scale was implemented from the 1920s through the 1960s with two main routes of production: the Lebedev process (one-step reaction) and the Ostromisslensky process (two-step reaction)[9,10]. In the two-step process, ethanol is dehydrogenated to acetaldehyde (eq 1.) in a first reactor and the ethanol/acetaldehyde mixture is converted to 1,3-BD (eq.2) in a second reactor. This allows achieving high selectivity by controlling (i) the temperature at which each reaction takes place and (ii) the ethanol to acetaldehyde molar ratio for (eq 2). In the one-step process, all these reactions (eq 1 and eq 2) take place in a single reactor. The overall reaction (eq 3) is that two molecules of ethanol yield one molecule of 1,3-BD, one molecule of hydrogen and two molecules of water (stoichiometric yield 0.587 tonne 1,3-BD/tonne ethanol). Also, numerous side products are formed[6], such as ethylene (eq 4) and diethyl ether (eq 5) from ethanol dehydration, n-butanol from condensation of ethanol (eq 6), butenes from n-butanol dehydration (eq 7), n-butanal from n-butanol dehydrogenation (eq 8) and heavy products (C_{6+}) from successive aldol condensation reactions of aldehydes and ketones (eq 9) formed in other side reactions [11,12]. It should be noted that there is not a consensus on the reactions involved in the formation of these side products and here just the simplest side reactions are provided for the reader's sake.

$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3\text{-}COH + H_2$ (eq 1)

$CH_3\text{-}CH_2\text{-}OH + CH_3\text{-}COH \rightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2 + 2H_2O$ (eq 2)

$2CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2 + H_2 + 2H_2O$ (eq 3)

$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2\text{=}CH_2 + H_2O$ (eq 4)

$2CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 + H_2O$ (eq 5)

$2CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH + H_2O$ (eq 6)

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH \rightarrow CH_2\text{=}CH\text{-}CH_2\text{-}CH_3 + H_2O$ (eq 7)

CH_3-CH_2-CH_2-CH_2OH→ CH_3-CH_2-CH_2-COH+H_2 (eq 8)

Aldehydes/ketones →C_{6+} products (eq 9)

The one-step process was developed in Russia, while the two-step process was developed in the USA and commercialized by Union Carbide and the Carbon Chemical Corporation. Both technologies became economically unfeasible due to the development of routes to produce 1,3-BD from petroleum-derived naphtha[5,9,13], with the exception of China and India, where they are still marginally used[6]. Since the cost of ethanol dominates the production costs, as concluded in this work, the most effective way to enhance the competitiveness of the process is to develop more selective catalysts in order to reduce consumption of ethanol per kg of 1,3-BD. That is the reason why in the last decade, the renewed interest in the production of 1,3-BD from ethanol has fostered the research of more selective and stable catalysts through a better understanding of reaction mechanisms, the required acid/base feature of the catalyst, the impact of preparation methods and the effect of reaction conditions[2,11,14–16]. Despite the great advance in catalyst development, the literature on the techno-economic and environmental assessment of one- and two-step processes based on this new generation of catalyst is scarce[1,17,18].

Only one techno-economic assessment (TEA) of the one-step process has been published[17], in the context of a bio-refinery with two parallel production lines, one for 1,3-BD and another for ε-caprolactam, both using C6 sugars as raw material and sharing a combined heat and power (CHP) system. The authors concluded that, for two different catalysts, an Au/MgO/SiO_2 catalyst[2], and an undisclosed catalyst, with 66 and 48% 1,3-BD selectivity, respectively, the 1,3-BD production is not economically viable since the production costs are 3-5 times higher than their reference market price (900 €/tonne). Regarding the environmental assessment of the one-step process, Shylesh *et al.*[2] evaluated the cradle-to-grave greenhouse gas (GHG) emissions of 1,3-BD production in the USA for different sources of ethanol, assuming that 1,3-BD is converted to SBR for automotive tires. The study was based on their Au/MgO/SiO_2 catalyst, with an estimated 94% overall carbon selectivity by recycling acetaldehyde to the reactor in order to promote (eq 2). They concluded that the GHG footprint of ethanol largely determines the environmental sustainability of the process so that a low-carbon ethanol source is the key to achieving a reduction in GHG emissions related to petroleum-derived 1,3-BD. In addition, substantial reductions in GHG emissions can be achieved by locating the 1,3-BD plants close to oil refineries in order to export coproduced hydrogen and take advantage of the petrochemical infrastructure. Cespi *et al.*[18] compared the cradle-to-gate life cycle assessment (LCA) of one-step and two-step processes, considering carbon footprint, cumulative energy demand (CED) and water consumption (WC) as environmental sustainability indicators. Inventory data for the LCA was extracted from a private report[19] where catalysts by BASF[20] and Daicel Corporation[21] were evaluated for the one and two-step processes, respectively. For different sources of ethanol (USA, Brazil, Europe), the environmental sustainability indicators for the two-step process were worse than those of the one-step process due to the larger amount of ethanol used in the former, probably because unconverted ethanol was burnt rather than recovered and recycled to the rector. An aggregate sustainability score showed that the one-step process using ethanol from Brazil produces the most sustainable bio-butadiene. It is worth noting that in these studies, the catalyst performance was not modeled under industrial operating conditions, considering the presence of impurities in the ethanol feed, i.e. both recycled by-products and water in the ethanol feedstock, that can strongly affect product selectivity and ethanol conversion[11,22]. Since the reactor performance dictates the design and performance of the plant, experimental data on catalyst performance under industrial conditions are necessary for an accurate TEA or LCA.

In the previous studies by our research group on ethanol conversion to 1,3-BD, we selected a mixed Hf-Zn catalyst[15] whose 1,3-BD carbon yield is one of the highest reported (~70%)[2,23–26]. The performance of this mixed Hf-Zn catalyst[15] was experimentally studied under industrial operating conditions for the one-step process[11,22]. The results revealed that the combined effect of water and temperature on catalyst performance is significantly important: water promotes the formation of undesired ethanol dehydration products (ethylene and diethyl ether) but also inhibits the formation of heavy compounds, which is favored at a high reaction temperature. This indicates that water content in the ethanol which is fed to the reactor should be a process design variable.

The aim of this work is to compare both the economic and environmental performance of a one-step process with the naphtha-cracking route for 1,3-BD production. The novelties of the work related to previous publications on 1,3-BD production from bioethanol are: (1) simulation of a one-step process using a reactor model built from data of a one-step catalyst performance under industrial operating conditions, which results in more accurate simulation of the industrial process; (2) Both TEA and LCA are performed on the same one-step process, so that its environmental and economic performance can be related, whereas in literature either TEA or LCA are only reported for different one-step processes; (3) The robustness of the LCA results of the one-step process are assessed by carrying out an uncertainty analysis.

On the basis of the experimental Hf-Zn catalyst performance under industrial operating conditions[11,22], a conceptual design of the one-step process was made and the resulting process, which is described in the Material and Methods section, was simulated with Aspen Plus V8.8[27–29]. The TEA and LCA of the proposed one-step process using the Hf-Zn catalyst were carried out from the mass and energy balances from the simulation. Historical market prices for 1,3-BD produced from naphtha-cracking route were used as references for assessing the profitability of the one-step process. The 1,3-BD naphtha-based production process included in Ecoinvent (V3) database was chosen as a reference case for the environmental sustainability analysis. A sensitivity analysis was performed in the economic study to evaluate the effects of the uncertainty in capital investment and the market prices of ethanol and 1,3-BD on the profitability of the one-step process. In the environmental study, three different cases were defined to take into consideration the influence of the geographical location of the one-step process plant: Brazil, USA and Europe. For each scenario, an uncertainty analysis of the LCA results was performed.

This article is part of a larger study which aims to assess the economic and environmental performance of both one and two-step processes for the conversion of ethanol to 1,3-BD using experimental data obtained by employing high-yield catalysts. Here, results for the one-step process are presented. The two-step process is under study and the results will be presented in a subsequent article along with a comparison with the one-step process.

MATERIALS AND METHODS

One-step process description and modeling

Software Aspen Plus V8.8 was employed to model the one-step process route for 1,3-BD production from hydrous ethanol (93 wt% ethanol). The conceptual design of the process was made by following the hierarchical method proposed by Douglas[30] and the Barnicki and Fair method for the separation train[31,32]. Here a brief and simplified description of the process is provided based on the block diagram shown in Figure 1. A more detailed description along with the one-step process flowsheet simulated in Aspen Plus V8.8 can be found in Section S2 of the Supporting Information. Fresh ethanol is mixed with a recycle stream of purified ethanol, which contains some impurities (water and by-products), and the mixture is fed to a furnace reactor. The reactor effluent is cooled to separate the condensable fraction or crude recycled ethanol (unconverted ethanol, water, acetaldehyde, butanal, acetone, butanol and heavy compounds) from light gases (hydrogen, ethylene, propylene, butenes and 1,3-BD). Ethanol is used to absorb 1,3-BD from the light gases together with butenes and light polar compounds (Figure 1, Reaction and separation). Next, 1,3-BD is desorbed from ethanol, together with butenes and light polar compounds (mainly acetaldehyde), resulting in crude butadiene. Acetaldehyde is removed from crude butadiene by washing with water before extractive distillation with dimethylformamide (DMF) (Figure 1, Butadiene purification), by which butenes are separated from 1,3-BD, to produce polymer-grade 1,3-BD (99.9 wt% purity and acetaldehyde concentration lower than 10 ppm)[33]. On the other hand, the crude recycled ethanol is sent to a liquid-liquid extraction column (Figure 1, Removal of heavy compounds), where heavy compounds are extracted with an organic solvent (octane) so that the subsequent recovery of ethanol by distillation is not hindered by their presence[33]. Fresh water is also fed to the extraction column to enhance the recovery of ethanol. The extracted heavy compounds are used as fuel in the plant while the clean recycled ethanol is sent to a distillation train where water and other polar compounds are separated from ethanol (Figure 1, Separation of polar compounds). As a result of these separations, several streams are obtained: i) a purified recycled ethanol (7.5 wt% water), which is sent to the furnace reactor; ii) an acetaldehyde stream of high purity as co-product, which is partially recycled to the reactor; iii) a mixture of the rest of the separated polar compounds, which is used as fuel in the plant (residual fuel); iv) polluted water with polar compounds, which is sent to a Fenton process for wastewater treatment[34].

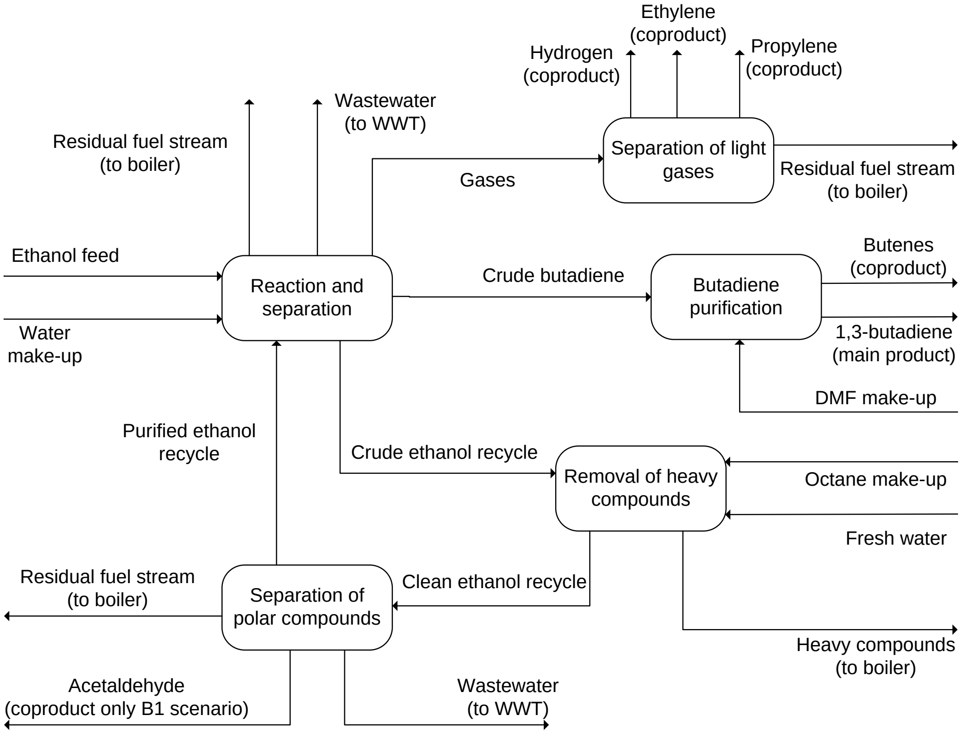

Figure 1. Simplified block diagram of the Ethanol-to-Butadiene process.

Finally, the light gases from the reactor (Gases), which comprise hydrogen, ethylene and propylene, are separated by means of molecular sieves and high-pressure distillation to obtain highly pure hydrogen, ethylene and propylene streams (Figure 1, Separation of light gases). These light gases, along with separated acetaldehyde and butenes are sold as co-products.

For the simulation of the one-step process, an appropriate thermodynamic model was selected for each section of the plant (Wilson method for “Butadiene purification”, Soave-Redlich-Kwong for the “Separation of light gases” and NRTL for the rest of the plant). In order to reduce the impact of uncertainty in the parameters of the thermodynamic models on simulation results, the parameters of these models as well as the Henry constants for the NRTL method were validated or regressed using experimental data from DECHEMA[35], NIST-TDE[28,36], Perry Handbook[37] and elsewhere[38,39]. When the experimental data were not available, the parameters were estimated with predictive methods (UNIFAC). The calibrated thermodynamic models allowed for rigorous simulation of flashes, absorbers, distillations and extraction columns within Aspen Plus.

The catalytic reactor was modeled as a yield reactor based on experimental data. A detailed description of the reactor modeling is given in section S3 of Supporting Information. Two scenarios were considered when modeling the Hf-Zn catalyst performance. In the first scenario (B1), ethanol conversion and product selectivity from experiments by the authors with hydrous ethanol were employed as input to the reactor model. The chosen operational conditions for this scenario (reaction temperature, space velocity and water content in the ethanol which is fed to the reactor) are those for which the highest experimental per-pass carbon yield of 1,3-BD was reached (~48%)[22]. A method was implemented in the reactor model to modify the experimental ethanol conversion and product selectivity in order to consider the presence of polar compounds in the ethanol feed stream (see section S3 of the Supporting Information). This method uses data obtained by the authors in experiments co-feeding ethanol and polar compounds[11]. In the second scenario (B2), with the aim of assessing the effect of a more highly selective catalyst on the performance of the process, we used the operational conditions as well as ethanol conversion and product selectivity from De Baerdemaeker *et al.*[15], who reported the highest selectivity for the 1,3-BD obtained with a Hf-Zn-based catalyst (70% for a pure ethanol feed). Before being used as input in the reactor model, these experimental ethanol conversion and product selectivity were corrected to consider the presence of water in the ethanol feed stream (see Supporting

Information). The same water content in the ethanol feed stream as in scenario B1 was chosen as operational condition.

Finally, the heat exchanger network of the plant was designed by optimization with the tool Aspen Energy Analysis, which considers the trade-off between the costs of utility consumption and heat exchangers. High (HPS), medium (MPS) and low-pressure steam (LPS), cooling water (CW), low-temperature refrigeration (propane) and electricity were imported as utilities to satisfy the heat and power demand of the plant. Also, natural gas was used as fuel in the furnace reactor. Details on the heat integration methodology and the resulting heat exchanger network are provided in section S5 of the Supporting Information.

Economic assessment

The plant was designed for a production capacity of 200,000 tonne/year of 1,3-BD so that it could be supplied by one or several ethanol plants located nearby, considering the high-range size and/or density of ethanol plants in USA, Brazil and Europe [40–43]. The economic assessment involves estimating the capital (CAPEX) and operating (OPEX) expenditures of the process. The fixed capital cost comprises direct and indirect costs. The total direct costs (or total installed cost, TIC) were calculated by multiplying the aggregate purchase cost of the pieces of equipment (PEC) by an installation factor. Then, the indirect costs were estimated as a percentage of TIC[44] (Table S1). The purchase cost of each piece of equipment was calculated either by using the Aspen Economic Evaluator (AEE) tool of Aspen Plus[27,45], cost correlations[46,47] or on-line cost databases[48,49] and correcting the effect of inflation by using the CEPCI cost index.

The CAPEX was finally calculated by adding the working capital and the cost of the land to the fixed capital costs (Table S2). On the other hand, the OPEX comprised variable and fixed operating costs. The variable operating costs were calculated from the consumption of raw materials, utilities, catalysts, etc.; while fixed operating costs were estimated as a factor of the TIC, as shown in Table S3. Also, a fixed selling price was assumed for each co-product in order to calculate the income from its sale (Table S4).

To assess the economic performance of each scenario, the Minimum Butadiene Selling Price (MBSP, €/tonne) was chosen as an economic indicator, i.e., the selling price of 1,3-BD necessary to recover the capital investment with the desired rate of return at the end of the plant life, or in other words, that results in the net present value equal to zero. The economic assumptions that were applied in the cash flow analysis are shown in Table S2. Sensitivity analyses of MBSP to the uncertainty in estimation of capital investment (±30%) and ethanol costs, based on its historic market price (2008-2018)[50,51], were carried out.

Life cycle assessment

The LCA is an important tool for the screening and evaluation of the environmental sustainability of alternative bio-based chemical industries and its use has increased in recent years. In this study, an attributional LCA, based on the guidelines of the ISO 14040/44 standards[52,53], was carried out with the aim of estimating the main environmental burdens and contributors in the industrial 1,3-BD production from bioethanol. An additional goal was to compare the environmental impact of the 1,3-BD scenarios with the current 1,3-BD production from naphtha. LCA was modeled using SimaPro software (V8.5.2.0)[54]. A cradle-to-gate approach was applied, covering all the stages in the supply chain of 1,3-BD. The functional unit used as a basis for comparison was 1 tonne of produced 1,3-BD. The LCA system boundaries to produce 1,3-BD from ethanol are shown in the Supporting Information (Figure S1).

The results of the mass and energy balances from the simulation of the one-step process were employed as foreground inventory data for 1,3-BD production from bioethanol while the Ecoinvent (V3) database[55] was employed for the background information. On the other hand, the inventory data for the 1,3-BD production from naphtha was sourced from the Ecoinvent (V3) database. The ReCiPe2016 midpoint (H) V1.02 was applied as the characterization method in this work. This updated version of ReCiPe includes global characterization factors and not only European like the former ReCiPe2008[56]. Two impact categories included in this method are considered highly important for the analysis of bio-processes[18]: i) Global warming potential (GWP100) and ii) Water consumption (WC). In order to assess the influence of the biogenic carbon storage on the GWP100 results, the end of life of the 1,3-BD employed as SBR[57] for automotive tires was taken into consideration for this impact category assessment as suggested by Shylesh et al.[2]: 44% of tire material is burnt, 32.2% repurposed, 1.8% recycled and 22% landfilled. The cumulative energy demand (CED) is also considered a valuable screening indicator and it has been used since the 1970s[58]. The last version of the available method in SimaPro software for CED calculation (V1.10) was used. According to ISO 14040/44 guidelines[52,53], system expansion was applied.

Furthermore, three cases were defined to assess the influence of the geographical location of the production plant, considering the world's main suppliers of ethanol: The United States (USA), Brazil (BR) and Europe (EU)[59]. Those regions have three different supply chains: 100% corn-based ethanol from the US, 100% sugarcane-based ethanol from BR and a representative ethanol mix from EU with the following distribution: 45% from corn, 27% from wheat, 22% from sugar beet and 6% from rye[60]. Since wheat-based ethanol was not included in Ecoinvent V3 database, data for wheat-based ethanol produced in France[61] were employed instead. Besides ethanol, the plant location was also considered for other elements of the inventory, such as electricity, steam, natural gas, co-products, among others. To analyze the robustness of the LCA results, an uncertainty analysis was performed by using background data from literature, rather than from Ecoinvent (V3).

RESULTS AND DISCUSSION

Mass and energy balances

The results of the reactor model within the simulation are presented since reactor performance largely determines the energy and mass balance of the process. Table 1 shows the ethanol conversion and carbon product selectivity calculated by the reactor model based on corrections of the input catalyst data to the model. In the B1 scenario the correction of the input catalyst data is due to the by-products recycled with ethanol, mainly acetaldehyde (~8 wt%), which largely increases the selectivity of ethanol to 1-3 BD by promoting (eq 2) but also decreases ethanol conversion, since some acetaldehyde adsorbs on dehydrogenating sites of the catalyst, thus hindering (eq 1). Overall, the per-pass yield of 1,3-BD almost does not change. In the B2 scenario the most important correction of the input catalyst data is due to presence of water in ethanol since water adsorbs and blocks catalyst active sites, decreasing ethanol conversion, but also increases surface acidity by transforming active sites, thereby promoting ethanol dehydration (eq 4 and eq 5) and increasing selectivity to ethylene and diethyl ether[21]. In this scenario the concentration of by-products in the recycled ethanol is low, mainly acetaldehyde (~1.5 wt%), and its effect on catalyst performance is relatively small. Overall, the selectivity to 1,3-BD barely changes after the corrections but per-pass yield of 1,3-BD significantly decreases.

Table 1. Catalyst performance input data for modelling the reactor and results of reactor model.

	Input data		Model results	
Scenario	B1	B2	B1	B2
Operating conditions[a]				
Temperature (ºC)	380	360	380	360
Water in ethanol (wt%)	7.5	0	7.5	7.5
WHSV[b] (h^{-1})	1.12	0.64	1.12	0.64
Other impurities in ethanol (wt%)	0	0	11.3	2.9
Ethanol conversion (%)	96.5	98.8	81.9	87.1
Product carbon selectivity (%)				
Ethylene	8.70	10.00	9.85	14.62
Propylene	2.93	3.60	2.93	3.35
1-butene	2.70	2.50	2.70	2.07
1,3-BD	49.75	70.00	58.78	69.47
2-trans-butene	2.70	2.50	2.70	2.07
Acetaldehyde	11.59	2.40	8.13	4.08
Diethyl ether	1.30	1.40	1.29	2.64
Acetone	1.43	0.74	1.43	0.47
Butanol	0.23	0.06	0.23	0.07
Other polar compounds[c]	10.26	6.80	3.55	1.17
Heavy compounds[d]	8.40	0.00	8.40	0.00

[a] For input data, the operating conditions refer to those at which the catalytic test was performed. For model results, the operating conditions refer to those at which the reactor performance is estimated based on corrections of the input data; [b] Weight Hourly Space Velocity (h^{-1}) is defined as the ratio: mass flow of ethanol compound (kg/h)/load of catalyst (kg); [c] the numerous other light organic polar compounds observed in the experiments are lumped into n-butanal; [d] heavy compounds are modeled as dodecane.

The overall mass and energy balances of B1 and B2 scenarios are compared in Table S5. The higher 1,3-BD selectivity (c.a.+10%) and per-pass ethanol conversion (c.a.+5%) of the Hf-Zn catalyst in the B2 scenario in comparison with the B1 scenario has important consequences on both the mass and energy performance of the process. First, the overall productivity of 1,3-BD is larger: 0.400 vs 0.334 tonne 1,3-BD/tonne anhydrous ethanol, or equivalently, lower raw ethanol (17%) is necessary per ton of 1,3-BD in the B2 scenario. The lower amount of raw ethanol to be processed and the lower generation of by-products, which facilitates their separation, result in lower consumption of utilities and solvents. For instance, the consumption of water, which is used to remove acetaldehyde from crude butadiene, and octane, which is used as solvent for the removal of heavy compounds, largely decreases due to lower selectivity to acetaldehyde and lower formation of heavy compounds, respectively. The lower water consumption leads to lower amounts of wastewater to be treated. On the other hand, the DMF required in the extractive distillation does not vary significantly since in both scenarios the ratio of butenes/1,3-BD is small. Regarding utilities, the lower generation of by-products is reflected in the lower heat loads of the re-boilers (steam) and condensers (CW) of the distillation columns to separate them from ethanol and 1,3-BD. In addition, the lower rate of ethanol to be processed reduces the consumption of natural gas in the furnace reactor, which also operates at a lower temperature. Overall, the total energy consumption (heating and cooling demand) of scenario B2 (25.5 GJ/tonne 1,3-BD) is 12% lower than that of scenario B1 (29.1 GJ/tonne 1,3-BD). In the literature lower total energy consumption has been reported for one-step processes: Cespi *et al.*[18] reported 11.4 GJ/tonne 1,3-BD, Moncada *et al.*[17] reported values between 8.8-14.3 GJ/tonne 1,3-BD and Shylesh *et al.*[2] reported a total heating consumption of 6.2 GJ/tonne 1,3-BD. Apart from differences in process design, configuration and modeling, the main reason for lower energy consumption in Cespi *et al.*[18]and Shylesh *et al.*[2] is most likely the use of more efficient catalysts, and therefore, higher 1,3-BD overall productivity (0.511 and 0.550 tonne 1,3-BD/tonne ethanol, respectively). Certainly, the total energy consumption in our work and that of Cespi *et al.*[18] and Shylesh *et al.*[2] correlates very well (R^2=0.96) with 1,3-BD overall productivity (tonne 1,3-BD/tonne ethanol), assuming that in the case of Shylesh *et al.*[2] the ratio of heating consumption to cooling consumption is similar to ours. An exception is the work of Moncada *et al.*[17] (0.279-0.395 tonne 1,3-BD/tonne ethanol) who reported much lower energy consumption with 1,3-BD overall productivity. The reason might be that in their work the 1,3-BD plant was integrated within a bio-refinery, with a shared combined heat and power (CHP) system, and therefore, improved opportunities for heat integration.

To summarize, the use of a more highly selective catalyst results in an important reduction in ethanol and energy consumption, which are critical aspects in the subsequent economic and environmental analysis.

Economic assessment

Figure 2 shows a breakdown of the MBSP for each scenario. The MBSP is largely determined by the operating costs (Table S6), mainly the cost of ethanol (86.8-92.7% of MBSP for B2 and B1 scenarios, respectively) and utilities. Since in the B2 scenario the consumption of ethanol and utilities is lower, the resulting MBSP is also smaller (1721 €/tonne against 1927 €/tonne). In the B1 scenario, the revenues from by-products are larger (Table S6) but they do not compensate the higher operating costs. In both scenarios, the contribution of the capital investment in the MBSP (depreciation and return on investment) is not substantial (7.4%-8.3% of MBSP for B2 and B1 scenarios, respectively) since the annualized CAPEX is relatively small compared to the operating costs (Table S6). For the design capacity of 200 ktonne 1,3-BD/year, the specific CAPEX ranges from 0.9-1.1 M€/ktonne 1,3-BD.

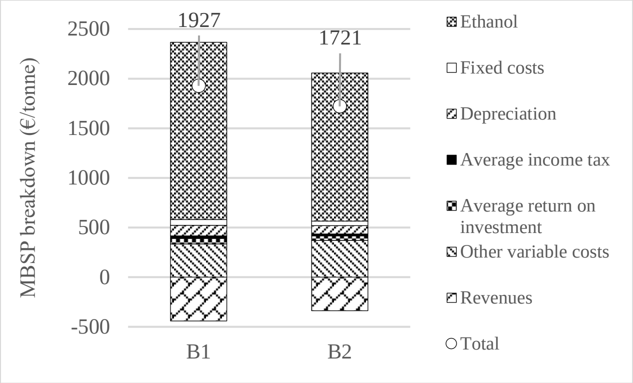

Figure 2. Breakdown of Minimum Butadiene Selling Price for each scenario. Figures over the bars indicate net MBSP, considering revenues from by-products.

The process is close to being profitable since the MBSP of scenarios B1 and B2 is only 1.13-1.26 times higher than the mean market price of 1,3-BD in the last 10 years (1529 €/tonne), respectively. Because the 1,3-BD and ethanol market prices are highly volatile[5], a sensitivity analysis was carried out where the price of azeotropic ethanol was changed within its upper and lower bounds in the last decade, and the resulting MBSP was compared with the 1,3-BD market price during the same period. In addition, the impact of the uncertainty in CAPEX estimation (± 30%) on the MBSP was assessed in the studied range of ethanol prices. The results of the sensitivity analysis are shown in Figure S2. The effect of the price of ethanol is substantial, as expected from the large share of ethanol costs in the MBSP. A change of 1 €/m^3 in the ethanol price results in an increase of 3.3 and 4.1 €/tonne in the MBSP for the B2 and B1 scenario, respectively. The higher sensitivity in the B1 scenario was expected as a large amount of ethanol is necessary per tonne of 1,3-BD. On the other hand, the effect of uncertainty in CAPEX estimation on MBSP is small, a change of ± 2.5 and ± 2.0% for B1 and B2 scenarios, respectively, since CAPEX has a relatively small influence on the MBSP, as mentioned before.

By comparing the MBSP with the 1,3-BD market price for both scenarios it was determined that the probability of the process to be profitable for the B1 scenario is relatively low, because the MBSP is greater than the mean 1,3-BD market price for almost the whole interval of the ethanol price (Figure S2). For the B2 scenario the situation is more favorable, but if the 1,3-BD price plummets to its lowest value (~850 €/tonne) the process is unprofitable regardless of the price of ethanol. The market prices of ethanol and 1,3-BD seem to be unrelated [5], so it is difficult to predict the profitability of this route. As explained in the next section, this route could lead to a reduction in the GHG emissions compared to the fossil-based route. If the savings in GHG emissions were subsided, the economics of this route might improve so that the production of 1,3-BD from ethanol were more appealing.

It is difficult to compare these economic results with those published so far in the literature by Moncada *et al.*[17]. The reason is that they evaluated 1,3-BD production from ethanol in the context of an integrated bio-refinery which previously produced ethanol from C_6 sugars as raw material. Consequently, they reported the economic results of the whole line of production, from sugars to 1,3-BD. With that in mind, they calculated a MBSP between 3406-4369 €/tonne, much higher than the average 1,3-BD market price, concluding the 1,3-BD production from C_6 sugars to be unprofitable. The MBSP was mainly determined by the cost of raw materials and the contribution of CAPEX to MBSP was marginal, which is similar to our results. They estimated a higher specific CAPEX, between 4-5.41 M€/ktonne 1,3-BD, because their production capacity was lower (24-34 ktonne 1,3-BD/year) and the investment of the entire line of production was considered.

Life cycle assessment

This section compares the environmental impacts (GWP100, WC, CED) of 1,3-BD production under the two studied scenarios, B1 and B2, in three different locations, The United States (USA), Brazil (BR) and Europe (EU). At the same time, these six cases are compared with the production of 1,3-BD from the steam cracking of naphtha. The inventories for the LCA models are shown in Table S7. Regarding the robustness of the LCA, the authors found that the inventory items that most contributed to the impact categories were related to ethanol and therefore only uncertainty in the background inventory data of ethanol was considered. However, the uncertainty values (e.g. standard deviation) of these inventory items were missing in the Ecoinvent (V3) database. This was indirectly addressed by using impact values related to the production of each type of ethanol (crop and region) reported in the literature for each impact category. More information on the literature sources and calculation of uncertainty in the impact values can be found in section S4 of the Supporting Information.

Next, the results for the GWP, WC and CED impact categories are presented and discussed. For each impact category, firstly, single-score results, obtained by using Ecoinvent (V3) background data, are analysed. Secondly, the robustness of the conclusions are assessed on the basis of the uncertainty study.

Global Warming Potential

Figure 3 depicts the single-score results obtained for the impact category GWP100 for each case. B2EU case is the best option in terms of GWP100 and, together with B1EU and B2USA cases, constitute the only three cases for which there is a reduction in this impact category with respect to the production of 1,3-BD from naphtha (8-26%). Ethanol production from biomass is largely the main contributor to the GWP100 for all scenarios, ranging from 65-84% of the total impact. Hence, for the same location B2 cases have a lower impact (10-14%) when compared to B1 cases. In addition, the location of the plant largely affects the GWP100 values, increasing them by 11 and 116% when it is placed in USA and BR, respectively, rather than in the EU, mainly due to the different ethanol sources. In this sense, according to the results, both the ethanol source and the catalyst efficiency are determinant factors in carbon emissions. As can be seen in Figure 3, other important contributors to GWP100 are energy consumption (steam) (2-14%) and hydrogen peroxide used in the wastewater treatment (2-9%). On the other hand, the generation of co-products (hydrogen, ethylene, propylene, butenes and acetaldehyde) reduces the total impact due to the obtained credits for avoiding their production in other processes. The credits are coming mainly from end-of-life (56-68%), followed by hydrogen (15-23%) and ethylene (7-10%). This indicates that the integration of the process with nearby facilities is important[2]. In addition, if the end-of-life practices are considered (see Life Cycle Assessment in Materials and Methods), GWP100 is reduced by 24-51% due to the resulting sequestration of biogenic carbon. All cases would show higher GWP100 than 1,3-BD from naphtha if carbon sequestration were not taken into account [2].

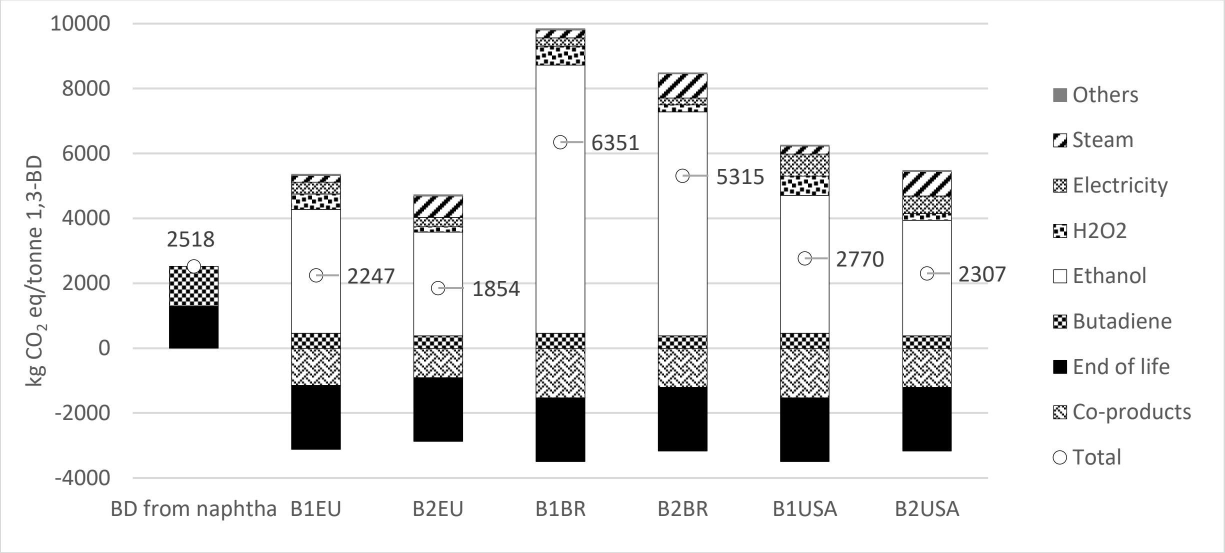

Figure 3. GWP100 considering the end-of-life of 1,3-BD as SBR. All background inventory data from Ecoinvent (V3) database.

The dependence of the outcome on the selection of the background date source reveals itself when comparing these results with those from the uncertainty analysis (Figure 4). It is remarkable that the use of Brazilian ethanol results in a higher probability of lower GWP100 score than using USA corn-ethanol or the European ethanol mix, just the opposite than concluded with the single scores. The reason is that the GWP impact values predicted from Ecoinvent V3 database (Table S12) for Brazilian ethanol is overestimated compared with the median value found in literature (2570 against 570 kg CO_2/tonne ethanol) because a very large contribution of the land use change impact is considered for Brazilian ethanol in the Ecoinvent[55] V3 database (1975 kg CO_2/tonne ethanol). Only for the B1BR and B2BR cases a reduction of emissions with respect to 1,3-BD from naphtha is very likely as the upper endpoint of the emission interval for those cases (2412 and 2025 kg CO_2eq/tonne 1,3-BD, respectively) is lower than the reference emission of 1,3-BD from naphtha (2518 kg CO_2eq/tonne 1,3-BD). Furthermore, net carbon sequestration is expected since the median of the GWP100 score is negative (-73 and -52 kg CO_2eq/tonne 1,3-BD for B1BR and B2BR cases, respectively). Therefore, Brazil would be the best option for the location of the plant in terms of GWP100 impact. Between USA and Europe, it cannot be clearly concluded which location is better because the European ethanol-mix shows lower median GWP100 score, in line with what was observed with single scores, but the interval of possible GWP100 scores for European ethanol mix is wider.

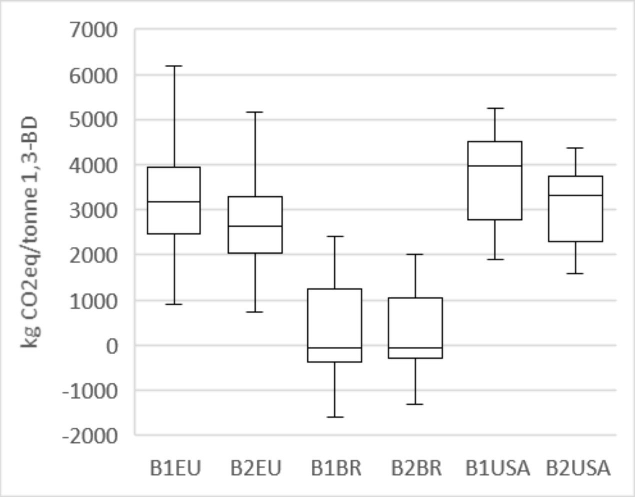

Figure 4. Uncertainty analysis of GWP100 using impact values of ethanol from literature. Median score for each case (kg CO_2/tonne 1,3-BD): B1EU (3187); B1BR (-73); B1USA (3976); B2EU (2640); B2BR (-52); B2USA (3314).

Water consumption

Regarding water consumption, the bio-scenarios present single-score results much higher than the naphtha-derived process, mainly due to the water used in crop cultivation for ethanol production, which ranges from 94 to 98% of total WC (Figure 5). Obviously, the WC score is lower (~18%) for the B2 scenario due to the lower consumption of ethanol with respect to B1. Under the same scenario, the WC scores for sugarcane (BR) and corn ethanol (USA) almost doubles that of the European mixed-crop ethanol (EU). The reason is the lower water consumption (m^3/tonne ethanol) in the cultivation of sugar beet (20.8), rye (169) and wheat (114) of the EU mixed crop compared to USA corn (262) and Brazilian sugarcane (287), according to Ecoinvent V3[55] database (Table S13). Regarding the influence of the ethanol source, all these results on water consumption are in accordance, in qualitative terms, with those obtained by Cespi *et al.*[18] but the absolute scores in our work are one order of magnitude larger.

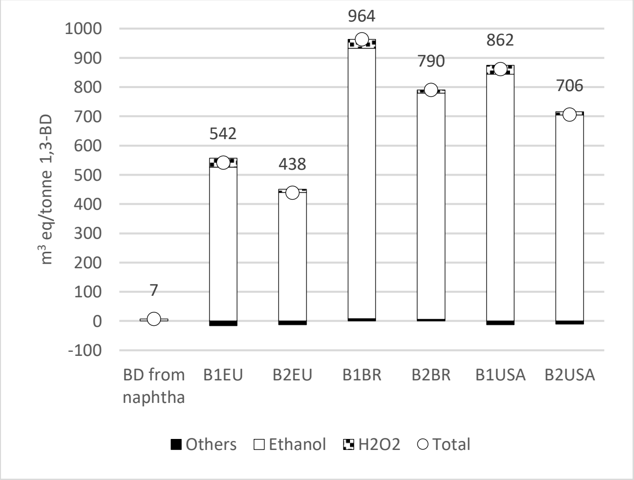

Figure 5. Water consumption score for each case. All background inventory data from Ecoinvent (V3) database.

The uncertainty analysis shows a quite different picture (Figure 6). First, the median water consumption for the Brazilian and USA ethanol cases are lower than that of the European ethanol mix, just the opposite that from single scores. The reason is the difference in the water consumption impact values from Ecoinvent database and the median value from literature for each crop-based ethanol (Table S13). A reason for the dispersion of scores observed for the three regions is the dispersion in irrigation water needed for crop cultivation within each region[62–65]. For instance, in USA one of the nine major bioethanol producing states (Nebraska) consumes ten-fold more liters of irrigation water per kg of ethanol than the other states[64,65], which partially explains the large score dispersion for USA cases. A lower dispersion is observed for Brazil cases since cultivation of sugarcane in Brazil is geographically concentrated in the South-Central region[41] leading to comparable irrigation needs[65]. Overall, Brazil seems to be the best option for the location of the plant in terms of water consumption impact, followed closely by USA.

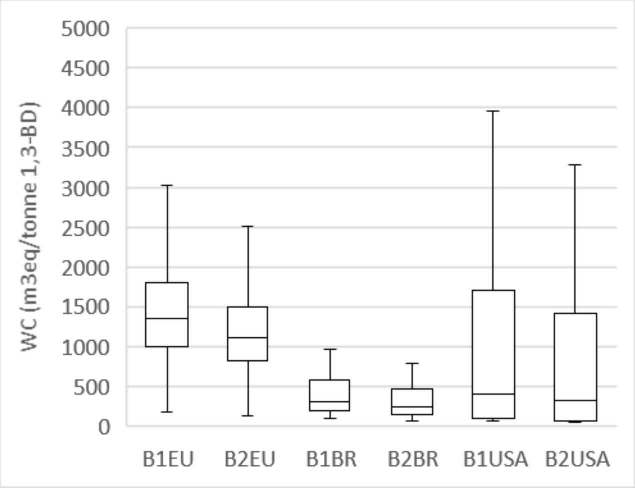

Figure 6. Uncertainty analysis of water consumption using impact values of ethanol from literature and Ecoinvent V3 itself. Median score for each case (m^3/tonne 1,3-BD): B1EU (1341); B1BR (299); B1USA (408); B2EU (1110); B2BR (235); B2USA (326).

Cumulative energy demand

The cumulative energy demand (CED) in the production of 1,3-BD from bioethanol is 50-250% higher than from naphtha (Figure 7). Most of the energy demand is ascribed to the ethanol supply chain (84-92%), and therefore, the location of the plant and the butadiene yield are important factors (B2 scenarios have 10-12% lower CED scores than B1 scenarios). The second most important contribution comes from the credits for the co-products (ethylene, hydrogen and acetaldehyde, in decreasing order) which reduces by 12-24% the energy demand of the bio-cases. These credits are larger for the B1 scenarios because the catalyst is less selective to 1,3-BD and the yield of co-products is larger. Finally, the fossil energy related to the generation of imported steam and electricity has a small share in the CED score.

USA is the best location of the plant in terms of CED since the USA cases present the lowest scores for both scenarios. The reason is that the supply chain of USA corn-ethanol has the lowest cumulative energy demand of all sources of ethanol, thanks to the high ethanol productivity of corn (0.329 tonne ethanol 95 wt%/tonne corn), which compensates the large (non-renewable) energy consumption in corn cultivation and conversion[55]. On the other hand, sugarcane shows the worst productivity (0.07 tonne ethanol/tonne sugarcane), which results in the BR cases having the highest CED score. Because the European crop mix, besides corn, consists of other crops with lower ethanol productivity than corn but higher than sugarcane (0.4 and 0.117 tonne ethanol 95 wt%/tonne of crop for wheat and sugar beet, respectively), the energy demand for the supply chain of European ethanol mix is between corn and sugarcane ethanol.

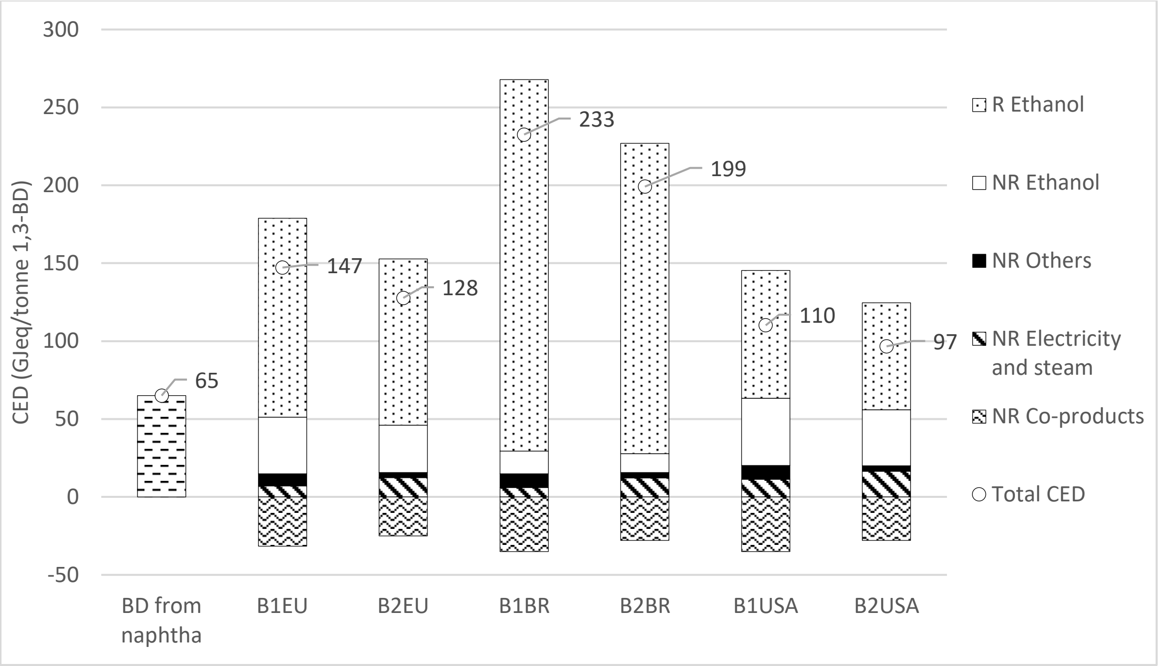

Figure 7. Breakdown of cumulative energy demand (CED) into renewable (R) and non-renewable (NR) energy.

The results of the uncertainty analysis (Figure 8) show that the median CED impact for the USA cases is lower than that of the European and Brazilian cases, resulting in the same conclusions on the best plant location than from single scores. The reason is that the impact values for ethanol from Ecoinvent database and the median value from literature for each crop-based ethanol are in general similar (Table S14). A large dispersion is observed for the European cases, which is consequence of the high variance in the ethanol yields found in literature for European wheat and corn.

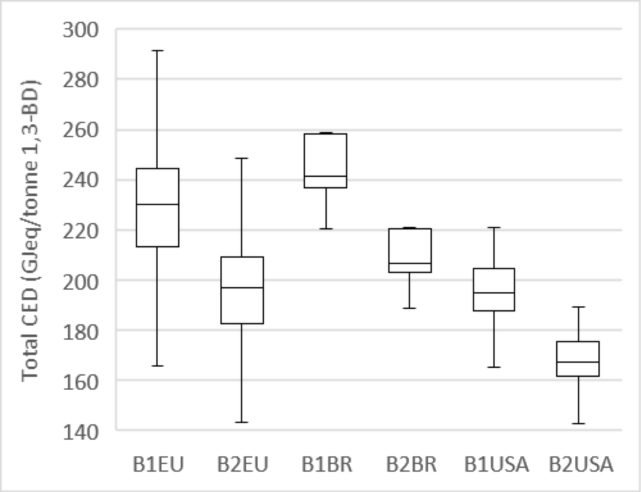

Figure 8. Uncertainty analysis of cumulative energy using impact values of ethanol from literature and Ecoinvent V3 itself. Median score for each case (GJeq/tonne 1,3-BD): B1EU (230); B1BR (241); B1USA (195); B2EU (197); B2BR (207); B2USA (168).

CONCLUSIONS

A process to produce 1,3-BD from ethanol in a one-step reaction with a Hf-Zn catalyst was designed using experimental data of the catalyst performance under industrial conditions, i.e, considering the presence of water and other by-products in recycled ethanol. The techno-economic and life cycle assessments of the process were performed and compared with the naphtha-cracking route. In the assessments two scenarios were defined to evaluate the impact of catalyst selectivity. In addition, for the environmental sustainability assessment, three further cases were defined to assess the influence of the geographical location of the production plant considering the world's main ethanol suppliers: The United States, Brazil and Europe.

The economic evaluation results suggest that 1,3-BD from ethanol is profitable when favorable combinations of market prices of ethanol and 1,3-BD are provided since the cost of raw ethanol dominates the production costs (c.a. 80%). The margin of profitability increases significantly with catalyst selectivity to 1,3-BD since a lower amount of ethanol is necessary per tonne of 1,3-BD. For a plant with a production capacity of 200 ktonne/year of 1,3-BD and considering the mean azeotropic ethanol market price of the last decade (450 €/m^3), an increase in 1,3-BD catalyst selectivity from 58 to 69% (+11 p.p) reduced capital investment from 222 to 180 M€ (-19%) and the minimum butadiene selling price from 1927 to 1721 €/tonne (-10.7%), but higher than the average butadiene market price (1529 €/tonne). Although the profitability of ethanol-to-butadiene depends on 1,3-BD and ethanol market prices the development of higher selective catalysts to reduce the consumption of ethanol per tonne of 1,3-butadiene is of paramount importance. Besides, the application of subsidies for reduction in GHG emissions in comparison with naphta-derived butadiene would make this route more appealing for commercialization.

In that sense, the environmental sustainability assessment shows that switching from naphtha-derived to bio-butadiene lead to substantial reductions in CO_2 emissions (GWP100) (8%-26%) but, in turn, to a significant increase in water consumption (62 to 137-fold) and cumulative energy demand (50-250%). Ethanol is the major contributor to all impact categories and therefore, the location of the plant and catalyst selectivity significantly affects the environmental sustainability of the process. In this sense, the increase in catalyst selectivity to 1,3-BD significantly reduces the environmental impact of the one-step process (a +11% increase in catalyst selectivity reduces CO_2 emissions by 10-14%, water consumption by 18% and cumulative energy demand by 12-14%). Therefore, the development of high selective catalysts is also important for the environmental sustainability of the process. Considering the three impact categories and the uncertainty analysis of the LCA results, the best plant location would be Brazil, with expected negative impact median value for GWP100 (-73 to -52 kg CO_2eq/tonne 1,3-BD) and the lowest median value for blue water consumption (235-299 m^3/tonne 1,3-BD) but the highest median value for cumulative energy demand (207-241 GJeq/tonne 1,3-BD), the latter due to the low ethanol yield of sugarcane.

Supporting Information.

Section S1: Supporting figures and tables for input data and results; Section S2: Detailed description of process flowsheet; Section S3: Description of reactor modeling; Section S4: Literature data for uncertainty analysis of environmental impacts; Section S5: Heat integration methodology and results

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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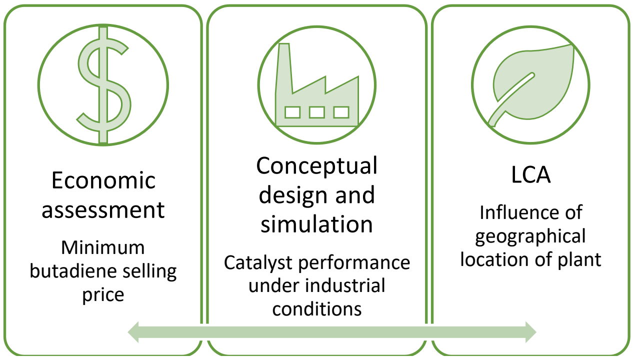

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