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Modeling and Analysis

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Production of bulk chemicals from lignocellulosic biomass via thermochemical conversion and syngas fermentation: a comparative techno-economic and environmental assessment of different site-specific supply chain configurations

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Abstract: This study presents the design and assessment of site-specific supply chains and related manufacturing processes for the production of bio-based chemicals from the syngas platform and via gasification of lignocellulosic biomass followed by syngas fermentation. The supply chains include feedstocks production and collection, biomass gasification, syngas fermentation, and downstream processing. For each of these stages, different alternatives were considered: four feedstocks (pine, corn stover, sugarcane bagasse, and eucalyptus), three products (ethanol, 2,3-butanediol and hexanoic acid), and three geographical locations (the Netherlands, the USA, and Brazil). Conceptual development and analysis of the supply chains were done through the combination of different design and assessment tools, namely biomass supply chains design, fermentation process design (based on thermodynamics and transport), process simulation, and economic and environmental assessments. The minimum selling price (MSP) and two environmental impact categories, i.e., global warming potential (GWP) and non-renewable energy use (NREU), were used as performance indicators. These were compared to data reported in scientific literature and commercial sources for similar processes and products. The best

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overall performance was obtained for the production of 2,3-butanediol from pine sourced in the USA. In the cases of ethanol and hexanoic acid, the syngas fermentation stage had significant contributions to MSP, GWP, and NREU, due mainly to its high energy requirements. Regarding the geographical location, the best economic performance was obtained for the USA followed by the Netherlands and Brazil respectively. Furthermore, operation in Brazil led to the lowest environmental impacts, followed by the Netherlands and the USA. © 2017 Society of Chemical Industry and John Wiley & Sons, Ltd

Supporting information may be found in the online version of this article.

Keywords: 2,3-butanediol; ethanol; hexanoic acid; biorefineries design; sustainability assessment; syngas fermentation; biomass gasification

Introduction

The continuous growth of global energy and materials demands, added to the consequent depletion of fossil resources, has given rise to concerns on how to guarantee a continuous supply of products while at the same time limiting the rise of the average global temperature to 2°C.[1] Thus, sustainable production of biofuels and biochemicals through novel routes has been encouraged to reduce dependency on non-renewable resources, better cope with volatility of crude oil prices, and mitigate growing greenhouse gas (GHG) emissions.[1,2] Feedstocks such as biomass and other short-cycled carbon sources, for example, CO, CO_2 and CH_4, are being investigated as possible replacements of petroleum and its derivatives.[3]

Currently, commercial-scale production of bio-based chemicals and fuels is mainly done from sugars, starch, and oil-containing crops, although ethical and moral debates have arisen since these feedstocks have traditionally been used for food and feed purposes. In contrast, waste and lignocellulosic biomass have no possible competition with food.[4]

Biomass can be processed through two main technological platforms, i.e., chemical/biochemical and thermochemical. The former is based on hydrolysis (e.g. enzymatic or chemical) of lignocellulose-producing sugars and other materials, while the latter is based on the thermochemical conversion of biomass producing a mixture of oils (tars) and gases.

Synthesis gas (commonly referred to as syngas) is the product of thermochemical gasification, a process carried out at temperatures ranging between 750 and 1000 °C. Syngas is a gas mixture containing mainly hydrogen, carbon monoxide, and carbon dioxide, and small fractions of methane, hydrogen sulfide, ammonia, and tars.[5] The composition of syngas depends highly on the type of feedstock, design of the gasifier, type of gasifying agent, and processing conditions.[6] Syngas is considered as one of the most prominent chemical platforms for biorefineries.[7] Syngas is currently mainly produced from fossil resources for heat and power generation or it is alternatively converted into fuels and industrial chemicals by catalytic Fischer-Tropsch synthesis[8] and fermentation[9] processes.

Acetogenic bacteria are commonly considered as syngas fermentation workhorses since they can utilize CO, H_2 and CO_2 as substrates by withdrawing electrons from H_2 and CO. Their carbon fixation into acetyl-CoA follows a metabolic route known as the Wood-Ljungdahl pathway.[9,10] These bacteria can then produce a variety of substances from syngas, for example acetate,[11] ethanol,[11] butyrate,[12] propionate,[13] butanol and hexanol,[14] 2,3-butanediol, lactate,[15] and polymers (*Rhodospirillum* bacteria).[16] Additionally, fermentation of syngas could drive the production of a wider range of products through further metabolic engineering[17,18] and bioprocess integration (e.g. toward medium chain fatty acids).[19]

The thermochemical conversion of biomass offers potential advantages over the biochemical route, for instance: (i) higher carbon yields, (ii) simpler process configuration, (iii) more flexibility on feedstock admission and product composition, and (iv) wider scale-up possibilities.[20,21] Moreover, fermentation also shows possible advantages over the catalytic conversion of syngas since microorganisms can (i) work under moderate temperatures and pressures; (ii) be more tolerant than chemical catalysts to poisoning by sulfur, tars, and chlorine; (iii) accept a wider range of gas compositions; and (iv) achieve higher conversions and yields.[8,9,22,23] Therefore, a hybrid process, combining thermochemical conversion of biomass and syngas fermentation, could help to reduce capital and operation costs as well as environmental impacts in the production of biofuels and bio-based chemicals.

Until 2016, two major companies were working to achieve commercial application of the syngas fermentation technology: INEOS Bio and LanzaTech. However, it was published that the former, which uses lignocellulosic biomass and municipal solid waste as feedstocks for gasification, has produced 'very little' ethanol from its 30 million L y^{-1} plant due to cyanide toxicity, and is currently selling the plant (Sapp M (www.biofuelsdigest.com)). On the other hand, LanzaTech, which uses mainly CO-rich flue gases from steel industry,[9] seems to have successfully developed fermentation technology, since it has signed an agreement with Primetals and ArcelorMittal for the design of a $96 million producing facility, which will be constructed in the latter's steel plant in Ghent, Belgium (http://corporate.arcelormittal.com). Production is expected to start by mid-2017. This is the first 47-kton-per-year project to produce ethanol via gas fermentation to be built in Europe (Lane J (www.biofuelsdigest.com)).

Although the syngas fermentation platform has received significant attention in recent years, there is still limited information available regarding integrated assessments of technical, economic, and environmental aspects of syngas production from lignocellulosic biomass and its subsequent fermentation into biochemicals and biofuels.[24–27] Therefore, this study presents the design and assessment of entire site-specific supply chains and manufacturing processes (biomass production and delivery, biomass gasification into syngas and cleaning, syngas fermentation into bio-based products, and final recovery and purification) for the production of three bio-based products: ethanol, 2,3-butanediol, and hexanoic acid. For the design of the site-specific supply chains, three locations and four feedstocks are considered: Brazil (with sugarcane bagasse and eucalyptus wood as feedstocks), the USA (with forestry residues and corn stover as feedstocks), and the Netherlands (where these four feedstocks can be imported for further processing into the three bio-based products). The techno-economic and environmental assessments were performed to evaluate and compare the effects of different processing configurations and operating conditions at multiples stages of the supply chains. Finally, a sensitivity analysis was performed to both analyze the robustness of the designs and identify possible improvements.

Methodology

A combination of different methods was applied to develop the conceptual designs of the supply chains and processes, and also to perform the techno-economic and environmental assessments. A detailed explanation is provided in the following sub-sections.

Supply chain and process design

The supply chains considered in this study consist of four processing stages: biomass supply, gasification, syngas fermentation, and downstream processing (DSP). Data concerning the type of operations and processing conditions were obtained from scientific literature on experimental work at either laboratory or pilot scale.

The production scale for ethanol production was defined from an average plant producing second-generation bioethanol, i.e., 240000 m^3 y^{-1} (189.4 kton y^{-1}) (Hoagland K (biomassmagazine.com)). In the cases of 2,3-butanediol and hexanoic acid, the production scales were set considering that the input of syngas to the fermentation unit was the same as for the ethanol production, in order to establish a common ground for comparison. Therefore, the required biomass supply was calculated accordingly for each case (each type of biomass has different yields to syngas as explained in the following two sections).

Biomass supply

Different biomass supply configurations were designed considering four different feedstocks: forestry residues (FR) and corn stover (CS), produced in the USA (US) and sugarcane bagasse (SB) and eucalyptus wood (EW), produced in Brazil (BR). The Netherlands (NL) has been included only as a location for processing, which means that biomass is imported from the other two locations and then processed first into syngas and then into one of the bio-based products. The four feedstocks were selected based on availability on the production site, price, and composition.

For the design of the biomass supply chains, the approach proposed by Hamelinck *et al.*[28] was adopted to obtain supply costs, environmental impacts, and energy requirements for the delivery of the lignocellulosic biomass.[29–31] Three main process operations were considered to structure the (inter)national biomass supply: (i) biomass production (seeding, land establishment, land maintenance and collection/harvesting); (ii) conditioning (chipping, baling, palletization, and drying); and (iii) transportation (truck, train and ship transport).[28] The sequence of operations was defined based on generic theoretical chains which contain five transfer points as shown in Figure 1:[3,28,32] (1) the production site, (2) a central gathering point, (3) a transport terminal for export, (4) a transport terminal for import, and (5) the conversion plant. In the specific

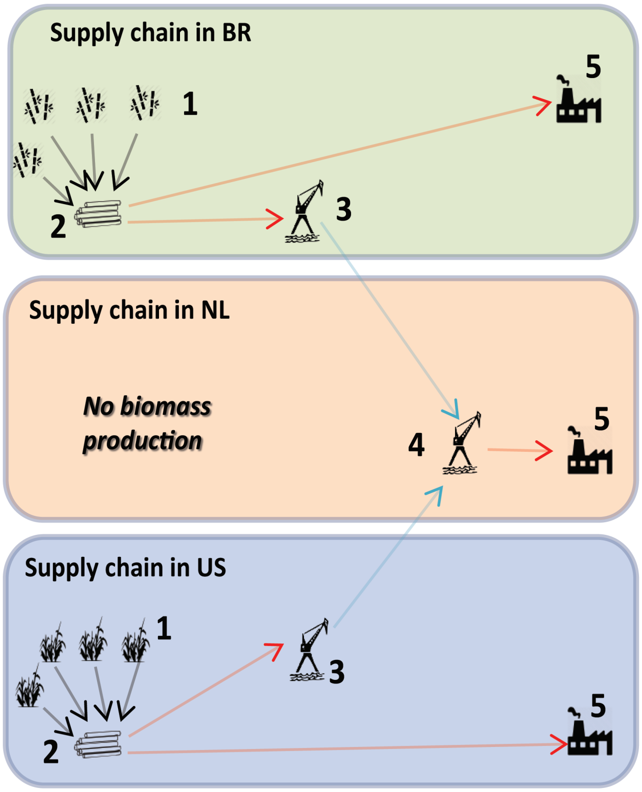


Figure 1. Configuration of supply chains according to the geographical location. Arrows represent transport by truck (black), train (red), and ship (blue). Transfer points are: 1. Biomass production site; 2. Central gathering point; 3. Export terminal; 4. Import terminal; and 5. Conversion plant (biomass to syngas and syngas to bio-based fuels and chemicals).

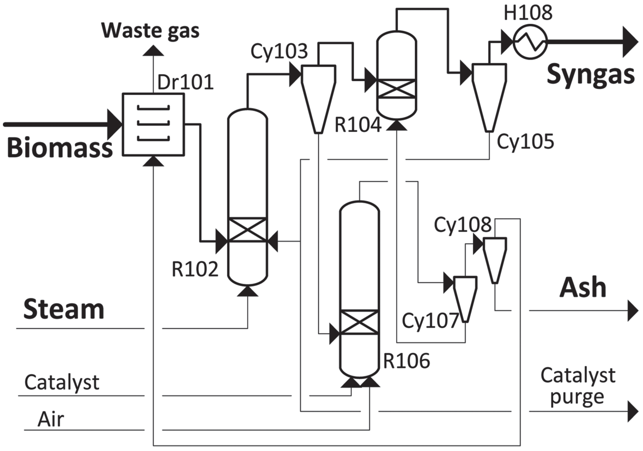


Figure 2. Process flow diagram for syngas production from biomass. Dr101: dryer; R102: gasifier; R104: reformer; R106: combustor; Cy: cyclones; H: heat exchangers.

case of international transport, pelletizing of biomass is included to increase its density and make long distance transportation more efficient.[28,33] The location of the central gathering points was defined to reach minimum transport costs between the sites with the highest biomass productivities and the next transfer points (considering road infrastructure and cost-efficiency of the transport type). Determination of the ports was mainly based on infrastructure and scale. Thus, the ports were selected considering that Panamax ships were available to assure large scale biomass transportation.[28] Furthermore, the moisture content of biomass entering the gasification unit is set to be 10 wt.% (reported as the optimum to minimize size and operation costs of the gas-to-liquid plant).[20,34,35]

Thermochemical conversion

The gasification process here considered was based on the technology described by the NREL,[34] which produces syngas suitable for fermentation. Such a process configuration returns low dilution of fermentable gases, and produces high carbon conversion into CO while keeping low CO_2 concentrations and maintains CH_4 as low as possible.[36] The process takes place at atmospheric pressure and uses three fluidized bed reactors, as shown in Fig. 2: an indirectly heated (allothermal) gasification reactor (R102), a combustion reactor (as heat source) (R106), and a gas conditioning reactor (R104). The gasification and combustion reactors operate with circulating fluidized beds (CFB) while the gas conditioning reactor uses a bubbling fluid bed (BFB). The indirectly heated dual CFB gasifier is considered the most suitable option for biomass conversion into syngas (for fermentation) due to syngas composition (rich in H_2 and low in CO_2), high carbon conversion, low tar production, flexibility on the type and particle size of fuel accepted, and scale-up potential.[37] Furthermore, olivine which is used as bed material (and catalyst), circulates through the three reactors (Fig. 2) and is (re)heated in the combustion reactor where char is burned with air.

The gasification process was simulated in Aspen Plus V8.8 using the physicochemical characterization presented in Table 1 for all feedstocks. The developed simulation model is based on a general approach to represent a dual fluidized bed gasifier known as fast internally circulating fluidized bed.[38] The model considers the following assumptions: the ideal gas law applies for the gas phase; operation takes place isothermally and at steady state; distribution of all components within the gas – bed material emulsion phase is homogenous; drying and gasification are instantaneous; no pressure drops or heat losses;[39] chemical equilibrium is assumed; since CH_4 represents the

Table 1. Biomass data: physicochemical characterization, production 1 requirements and 2 production costs

Characteristics	Forestry residues Pine wood (PW)	Agricultural residues		Energy crops Eucalyptus wood (EW)
		Sugarcane bagasse (SB)	Corn stover (CS)	
Region of production	US	BR	US	BR
Commodity shape	Chips	Fines	Bales	Logs
Moisture content$_{\text{green biomass}}$ (wt.%) [a]	45[3,32]	51[42]	24[32,43,44]	45[32,45]
Ultimate analysis (wt.%)				
Ash	0.6[46,47]	3.2[48,49]	6.0[44,50]	3.4[47,51]
C	49.7[46,47]	45.2[48,49]	47.3[44,50]	46.0[47]
H	7.8[46,47]	5.5[48,49]	5.1[44,50]	5.8[47]
O	41.8[46,47]	40.7[48,49]	40.6[44,50]	44.5[47]
N	0.1[46,47]	0.1[48,49]	0.8[44,50]	0.3[47]
S	0.05[46,47]	0.05[48,49]	0.22[44,50]	0.0[47]
Proximate analysis				
Volatile matter (wt.%)	82.3[46,47]	83.7[48,49]	54.6[44,50]	75.4[47]
Fixed carbon (wt.%)	17.2[46,47]	13.2[48,49]	7.15[44,50]	21.3[47]
HHV [b] (GJ $\text{ton}_{\text{dry}}^{-1}$)	20.2[51]	18.8[51]	19.0[51]	18.6[51]
Avg. particle size (mm)	30	10	10	30
Density (kg $\text{m}_{\text{bulk}}^{-3}$)	473[52]	175[53]	500[54,55]	380[56]
Biomass production				
Average yield (t km^{-2} y^{-1})	164[3]	8500[57,58]	516[59]	2810[60,61]
Cultivation land required (km^{2})	3428	214	773	196
Herbicide requirements (kg km^{-2} y^{-1})	0.164[3]	220[62]	235[63]	0.84[63]
Fertilizer requirements (kg km^{-2} y^{-1})	16.4[3]	29000[58]	31270[59]	48[63]
Total diesel consumption (kg km^{-2} y^{-1})	0.64[3]	24.7[58,64,65]	8.6[66]	26.8[3]

[a] Green biomass is defined as wet biomass at its harvesting phase.
[b] HHV: Higher heating value.

major part of hydrocarbons, the presence of longer chain hydrocarbons is neglected;[40,41] all nitrogen and sulfur in biomass are converted into NH_3 and H_2S; and char only consists of carbon and ash.

For the gasification process, steam (at 450°C and 1 bar) is fed to reactor R102. This steam has a double function: it is the fluidizing medium and the oxidizing agent for gasification and tar reforming (Table 2). The mass flow rate of steam is defined by the steam to biomass ratio which is set at 0.75.[38] The gasification reactions (Table 2) take place when high temperatures are reached (850°C).

In the tar reforming process, the gas coming from the gasifier is sent to the catalytic tar reformer (R104), where methane and higher hydrocarbons are oxidized into both CO and H_2, while CO into CO_2, and NH_3 converted into both N_2 and H_2 (Table 2).[37,67] Steam addition to the tar reformer was excluded from the model since the water content in the input gas was already sufficient to drive the reactions and avoid additional costs and gas dilution.

Fermentation

The three fermentation products here analyzed were selected from an initial list of nine components as introduced in the first section (acetate,[11] ethanol,[11] butyrate,[12] propionate,[13] butanol, hexanol,[14] 2,3-butanediol,[15] lactate,[15] and polymers[16]). For this selection, three main criteria were considered: (i) published experimental achievements considering techniques, yields, titers, and productivities; (ii) energy and mass requirements, and waste generation from possible DSP routes; and (iii) global market size of products. Thus, 2,3-butanediol, ethanol, and hexanoic acid were selected as the most attractive syngas fermentation products. The expected uses of ethanol and hexanoic acid are as biofuels either for blending or

Table 2. List of reactions for: Gasification, tar reforming, syngas fermentation and carboxylic acid chain elongation.

Process	Reaction	Reaction number
Gasification	$CH_aO_bN_cS_d^* + eH_2O \rightarrow n_1C + n_2CO + n_3CO_2 + (a/2)H_2 + (c/2)N_2 + dS$	(1)
	$C + H_2O \rightarrow CO + H_2$	(2)
	$C + 2H_2O \rightarrow CO_2 + 2H_2$	(3)
	$C + CO_2 \rightarrow CO$	(4)
	$C + 2H_2 \rightarrow CH_4$	(5)
	$CO_2 + H_2 \rightarrow CO + H_2O$	(6)
	$N + 1.5H_2 \rightarrow NH_3$	(7)
	$S + H_2 \rightarrow H_2S$	(8)
Tar Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	(9)
	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	(10)
	$CO + H_2O \rightarrow CO_2 + H_2$	(11)
	$2NH_3 \rightarrow 3H_2 + N_2$	(12)
Ethanol production	$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2$	(13)
	$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$	(14)
2,3-butanediol production	$11CO + 5H_2O \rightarrow C_4H_8(OH)_2 + 7CO_2$	(15)
	$4CO_2 + 11H_2 \rightarrow C_4H_8(OH)_2 + + 6H_2O$	(16)
Microbial growth	$2CO + 0.5H_2O + 0.25NH_4^+ \rightarrow CH_{1.75}O_{0.50}N_{0.25} + CO_2 + 0.25H^+$	(17)
	$2H_2 + CO_2 + 0.25NH_4^+ \rightarrow CH_{1.75}O_{0.50}N_{0.25} + 1.5H_2O + 0.25H^+$	(18)
Ethanol oxidation	$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$	(19)
Chain elongation	$C_xH_{2x+1}COOH + C_2H_5OH \rightarrow C_{x+2}H_{2(x+2)+1}COOH + H_2O$	(20)

* Biomass

direct combustion;[9,68] however, ethanol has also shown to be a prominent chemical building block for further conversion to value-added products.[69] Furthermore, hexanoic acid can also be used for manufacturing of food additives (esters).[70] 2,3-butanediol is considered as a precursor for multiple chemical products including solvents.[15] Additionally, one co-product was assumed to be produced by each one of the three fermentations here considered: acetic acid, ethanol, and butyric acid, for ethanol, 2,3-butanediol and hexanoic acid production, respectively.

The fermentation stoichiometry and kinetics were predicted through thermodynamics.[71,72] The Gibbs free energy dissipated via the catabolic reactions inside the cell (Eqns (13) and (14) are examples for ethanol production) was used to calculate the amount of substrates consumed for microbial growth (Eqns (17) and (18)). For ethanol production, the distribution of carbon among main product and the co-product was adjusted according to published experimental results at laboratory scale. For 2,3-butanediol and hexanoic acid production, the amount of co-product generated was set in similar values than ethanol production. The maximum specific substrate consumption rate was estimated assuming that the amount of Gibbs free energy is collected from the electron donor, at a maximum rate determined by the capacity of the electron transport chain (3 mol electrons per carbon mol of biomass per hour).[72] With this value, the common microbial energy needs for maintenance and the biomass yield on the carbon source, the maximum growth rate was calculated using Herbert-Pirt equation for anaerobic growth.[72] Additionally, considering that the catabolic reactions must produce at least 15 kJ mol^{-1} in order to maintain an active a proton motive force across the membrane, the affinity constants of electron donors were assumed to be close to the concentrations at which the catabolic reaction produces that minimum of Gibbs free energy.[72] All Gibbs free energies of reactions were adjusted to the fermentation conditions of temperature, pH, and concentrations of substances involved in the metabolic black-box model. Electron transport capacity and microbial energy needs for maintenance were also adjusted to the operation temperature. For a detailed description on the procedure followed to determine stoichiometric and kinetic parameters of the three fermentations, as well for the fermentors design, please see Supporting Information.

Ethanol and 2,3-butanediol are produced directly from syngas fermentation.[9,15] The H_2/CO ratio in which the syngas is fed to the fermentation defines the microbial stoichiometry, and thus water and CO_2 can either be consumed or produced (Eqns (13)–(16)). For both fermentations, the processing conditions used were 37°C, 1 bar (top pressure) and pH of 5. The resulting concentrations of gases and biomass were obtained from mass balances and calculated by using the mass transfer capacities (MTC) inside the fermentors. The MTC were calculated for each gaseous substrate and defined from superficial gas velocities and the compound solubilities under actual P-T conditions and the gas phase composition.[73]

The syngas fermentors were designed as bubble columns using three main constraints: a maximum liquid volume of 900 m^3, maximum vessel height of 22 m, and gas hold-up of 15 vol.% max.[73] In ethanol production, the amount of syngas required to achieve the maximum hold-up was enough to remove all ethanol produced by evaporation. This amount which resulted in around 400 vol.% stoichiometric excess, also guaranteed sufficient CO and H_2 MTC required by microbes.

Hexanoic acid was assumed to be anaerobically produced from ethanol and acetic acid which are generated in a previous syngas fermentation stage.[19] The synthesis of this carboxylic acid couples an ethanol oxidation reaction with a chain elongation reaction (Eqns (19) and (20)). The fermentation conditions were set to be 30°C, pH 5 and low pressure (0.045 bar) to ensure low H_2 concentration at the bottom of the reactor, hence allowing the ethanol oxidation to be thermodynamically feasible.

The chain elongation reactor was conceptualized to operate close to vacuum conditions and was designed as a bubble column; although it does not have any gas input, the broth mixing is achieved through the combined effect of H_2 production and water evaporation. Three key constraints were here used for the fermentor's design: liquid volume not larger than 2000 m^3, maximum 15 vol.% gas hold-up at the top of the reactor[73] and a gas–liquid mixture height that would avoid inhibitory H_2 concentrations at the bottom of the vessel.

Downstream processing

Different purification routes have been designed for each of the three chosen products, as shown in Figure 3.

In the case of ethanol production (Figure 3(a)), ethanol is continuously removed from the syngas fermentor (R201) by the gas excess. The resulting stream is compressed (P202) to 3.2 bar and cooled to −7 °C (C203) to condense a mix of water and ethanol. This mix is separated from the gases by flashing (F204), leading to a 61 wt.% ethanol concentration and 96 % recovery. The gas stream containing carbon dioxide and non-consumed CO and H_2 is treated in a monoethanolamine (MEA)-based process to remove the CO_2.[74] The remaining fractions of CO and H_2 are mixed with fresh syngas and then fed back to the fermenter. The pre-concentrated ethanol stream is pre-heated (H301) for an azeotropic distillation (D302); the bottoms stream (containing water, ethanol, and acetic acid) is sent back to the fermentor while the top stream follows a dehydration process by adsorption (A401). Thus, 95% of water is removed by the molecular sieve,[75] while the ethanol stream is condensed (C302) and cooled (H303) to storage temperature. The resulting product contains 0.27 wt.% water, while 5.5 % of the product is lost through the DSP. The adsorption units (I205) are used to remove acetic acid through ion exchange.[76]

Contrary to the ethanol DSP, 2,3-butanediol (Figure 3(b)) is continuously removed from the syngas fermentors (R201) in the liquid phase. Microfiltration (S204) is used first for biomass retention[77] and subsequently water is partially removed by reverse osmosis (RO302) at a flux of 45 kg m^{-2} h^{-1}).[78] The product is concentrated up to 390 g L^{-1}, while the losses across the membrane account for 3.9%.[78] The permeate is recycled back to the fermentation tank, while the retentate is subjected to distillation (D303) to separate water and ethanol. The resulting bottoms stream is furtherly flash evaporated (H401) to eliminate dissolved solids carried from the fermentation. 2,3-butanediol is finally condensed (C402) and cooled (H403) to storage temperature. The final product purity is 99.8 wt.% (the remaining 0.2 % is water) with an overall recovery of 99.9%. Similarly as for the ethanol DSP, this DSP also includes CO_2 removal (by the MEA-based process)[74] from the recycling of off-gas due to its partial consumption during fermentation stage.

The DSP for hexanoic acid (Fig. 3(c)) starts at the chain elongation reactor (R301) where it is produced from ethanol and acetic acid. The off-gas stream from the chain elongation reactor is partially dehydrated by condensation

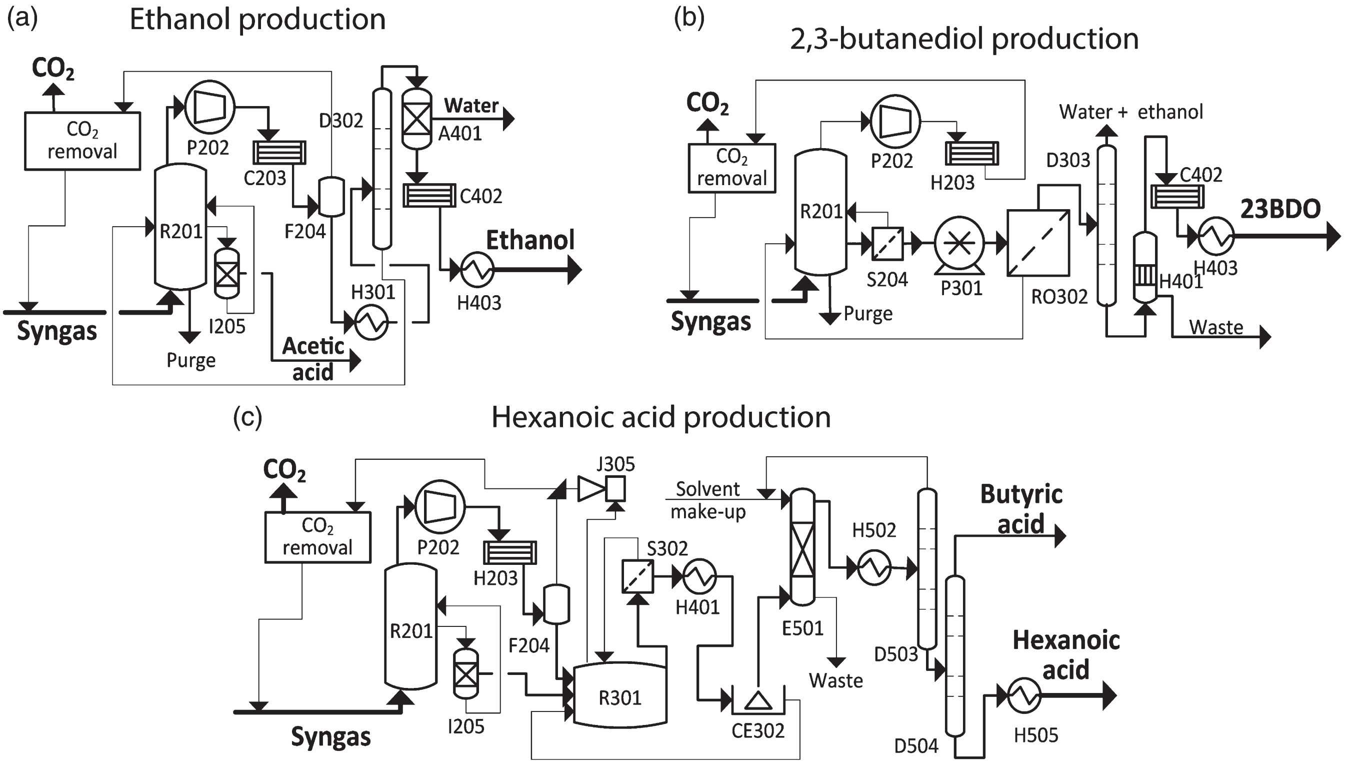


Figure 3. Process flow diagrams for syngas fermentation and DSP for producing: (a) ethanol, (b) 2,3-butanediol, and (c) hexanoic acid.

(C303) and flashing (F304), and then it is directed to an ejector (J305) to generate the vacuum conditions needed for fermentation.[79] The water content (from the steam ejector), temperature and pressure of the off-gas are adjusted before it is recycled back to the syngas fermenters. This recycling helps to improve the CO_2 consumption due to the increase in the H_2 supply. The organic liquid products of the elongation reactor may form a stabilized emulsion with the aqueous phase[80] which is then separated by microfiltration (S302).[77] The latter process is also used for biomass retention. The oil–water emulsion is ultimately destabilized by thermal treatment (cooling below the acid's freezing point),[81,82] and the two phases are separated by centrifugation (CE402). The inorganic phase is warmed up and recycled back to the chain elongation reactor to provide part of the heating required by the fermentation, while the organic phase (still with a 58 wt.% water content) is mixed with n-decane (E501) to separate the hexanoic acid from water and the polar impurities dragged along from the fermentation. The solvent is then removed and regenerated by distillation (D503), and recycled back to the extractor. Finally, the acids mixture is distilled to produce a hexanoic acid with a purity of 99.9 wt.% and with an overall recovery of 95.9%.

Economic evaluation

The economic analysis of the designed processes was based on the total production costs (considering both capital expenditures (CAPEX) and operational expenditures (OPEX)) and the minimum selling price (MSP) of products. The MSP was understood as the selling price that would bring the net present value (NPV) to zero at a defined number of years (payback time (PBT)), which for the base-cases was set at 5 years. CAPEX was based on multiple factors related to the total equipment purchase costs (EPC),[83] which in turn depends on individual equipment's characteristic size. The EPC of this study were adapted from multiple sources: the NREL's reports for all equipment used in the syngas production process[34] and also for adsorbers;[75,84] Seider *et al.*[85] for membrane-based operations and compressors; matche.com for fermentors; Husebye *et al.*[74] for the CO_2 MEA-based process; SuperPro Designer V9.0 for centrifuges; and Aspen Plus V8.8 for typical processing equipment such as distillation columns, extraction units, heat exchangers, evaporators, condensers and flash separators. When needed, the 6/10 scaling factor rule was used for capacity corrections.[83] In addition, prices for all equipment were updated to 2015 by using the Chemical Engineering

Plant Cost Index (CEPCI) (www.chemengonline.com), and the project lifetime was fixed at 15 years.

Aggregation of OPEX was based on Peters and Timmerhaus,[83] as follows:

- Facility-dependent cost (FDC): depreciation, maintenance, insurance, local taxes and overhead. The FDCs are calculated as a function of the EPCs.[83] Linear depreciation was assumed through the project's lifetime resulting in a salvage value equal to 10% of purchase cost. A yearly maintenance equal to 15% of EPC was also assumed.
- Process-related cost (PRC): Raw materials and utilities. Raw material flows and utilities requirements are derived from the mass and energy balances. Prices of raw materials were obtained from open websites (icis.com and alibaba.com), while the prices of utilities and industrial services were defined according to Vasudevan and Ulrich.[86]
- Labor: it was assumed to be 7% of both FDC plus PRC.

Furthermore, the economic performance for each case was adjusted to the different geographical locations here analyzed by using (i) location factors for CAPEX,[87] (ii) specific prices for fuels (used for defining prices of utilities)[86] and lignocellulosic biomass, and (iii) local economic indexes: interest rate and taxes on revenue. The used values are shown in Table 3.

Life cycle assessment (LCA)

The LCA was performed according to the guidelines ISO 14040 and 14044.[94,95] The goal was to estimate and compare the environmental impacts of the different supply

Table 3. Parameters of the economic model for comparison of the different geographical locations of the processing plants.

Model parameters	Value		
Project lifetime (y)	15		
Payback time (y)	5		
Debt time period (y)	10		
Debt-to-equity ratio	1		
Interest type	Compounded		
Inflation rate	0		
Depreciation type	Linear		
Salvage value	10 % of EPC		
Equipment maintenance	15 % of EPC		
Labor	7 % of (FDC + PRC)		
Working capital	1/12 of OPEX		
Start-up costs	22 % of OPEX		
Region-specific parameters			
Country	US	NL	BR
Location factor [87]	1.03	1.19	1.01
Fuel price ($ GJ^{-1})	5.075[88]	12.19[88]	4.220[b]
Electricity price ($ MWh^{-1})	70.14[88]	118.0[88]	134.9[c]
Interest rate (%)[a]	1.80	1.00	14.25
Tax on revenue (%)[a]	39.0	25.0	34.0
Cost of feedstock ($ ton$_{wet}^{-1}$) (at year)			
Pine wood	15 (2011) [89,90]	-	-
Sugarcane Bagasse	-	-	17 (2012) [91,92]
Corn stover	24 (2011) [32,59,93]	-	-
Eucalyptus wood	-	-	31 (2011) [32,45]

[a] www.tradingeconomies.com
[b] br.investing.com
[c] ANEEL.gov.br (http://relatorios.aneel.gov.br) * Biomass

chains, followed by a comparison with data reported in literature for the same products (or similar products with equivalent functionalities, depending on data availability) from first-generation and second-generation feedstocks and from fossil sources. A 'cradle-to-gate plus incineration' approach[96] was defined for the system boundaries which include feedstock's supply, syngas production, fermentation, and DSP stages. Additionally, to produce a fair comparison between the impacts of the products with fossil counterparts, the system was expanded to include the final combustion (neglecting its distribution) of the products. The environmental impact categories analyzed in this study were the primary energy use (calculated as non-renewable energy use, NREU) and the global warming potential (GWP) (determined as GHG emissions). The functional unit for the inventory analysis and the impacts assessment is the production of 1 kg of end product for 2,3-butanediol and hexanoic acid, while for ethanol, the unit used is 1 MJ calculated at its lower heating value (LHV: 29.7 MJ kg^{-1}).

Individual impact characterization factors for materials and energy carriers were taken from the Ecoinvent V2.2 database, literature, and internet references (Table 4). The environmental impacts data for sugarcane bagasse and corn stover were adopted from literature by applying economic allocation (used factors are: 0.18 for SB, and 0.21 for CS) since they are considered as waste materials.[97,98]

Sensitivity analysis

During the development of the conceptual designs of the supply chains and related processes, some assumptions for specific variables were adopted. A sensitivity analsysis is performed on the most critical variables to determine their influence on the techno-economic and environmental performances, and to identify opportunities for further improvements.

Three variables specifically apply to syngas production: (i) gasification temperature was varied from 650 °C to 1050 °C; (ii) the tar reformer unit in the gasification process was removed; and (iii) two possible uses for the heat produced in gasification was evaluated, i.e., generation of electricity or steam. The gasification temperature has been reported to have a strong influence on the syngas composition;[38] therefore its influence has been analyzed and subsequently optimized. Three other variables were studied for the fermentation stage: (iv) gas flow rate across the syngas fermentors (which has influence on the mass transfer capacity, and therefore on the productivity); (v) output concentration of products in the fermentation tank (which determines the size of the DSP operations); and (vi) the hexanoic acid production throughput (which is related to its application and market, and therefore its selling price). Finally, three variables directly influencing the economic evaluation have been considered: (vii) interest rate (which has shown variations during the past ten years in the three considered plant locations); (viii) fermentor purchase cost; and (ix) payback time of the investment (which relates to the risks that investors would be willing to take). The fermentor purchase costs were varied from half to the double of the base value used for each single equipment (M$3.7 and M$8.5 for the syngas and chain elongation fermentors, respectively); the interest rate was varied in the ranges 0.20–2.45% (for NL), 7.25–16.50% (for BR), and

Table 4. Individual impact characterization factors for materials and energy carriers for NREU and GWP.[a]

Component	Unit	NREU (MJ $unit^{-1}$)	GWP (g_{CO2eq} $unit^{-1}$)	Component	Unit	NREU (MJ $unit^{-1}$)	GWP (g_{CO2eq} $unit^{-1}$)
Diesel	MJ	1.19	11.2	Ammonia	kg	50.86	2929.4
Electricity (US)	MJ	2.13	188.8[c]	Process water	kg	0.08	6.6
Electricity (BR)	MJ	0.46	80.0[c]	KOH	kg	32.56	2240.7
Electricity (NL)	MJ	2.06	144.6	HCl	kg	6.60	397.0
Cooling water	kg	0.01	0.3	Decane	kg	77.24	2173.3
Heat [b]	MJ	1.56	100.5	Solid waste removal	kg	0.04	2.5
Fertilizer	kg	62.45	1571.6	Primary WWT	kg	0.12	18.6
Herbicide	kg	221.00	7930.0	Secondary WWT	kg	0.25	83.2
Olivine	kg	0.13	39.2	Microbial biomass combustion	kg	0.001	3.1

[a] Most data, excluding the referenced to footnotes, was obtained from Ecoinvent v2.2 database.
[b] Referred to all types of industrial heat, for example steam and, excluding cooling water. The same value is used for all locations.
[c] Calculated as a function of the renewable fraction in the national grid mixture[99] (http://www.tsp-data-portal.org) and taking the data for NL as reference for linear regression.

0.25–5.25% (for US); while the payback time was analyzed for 3 to 7 years.

Results and discussion

Process design

The biomass supply chains were designed to produce syngas with a composition that is suitable for fermentation into chemicals.[36] Table 5 shows the resulting yields of syngas on biomass and the composition of the resulting syngas for each feedstock. The highest syngas yield is obtained from pine wood because of its high hydrogen content and low presence of ash and nitrogen compared to the other feedstocks. This syngas yield has, in general, a low variability (i.e., +/– 5.3%).

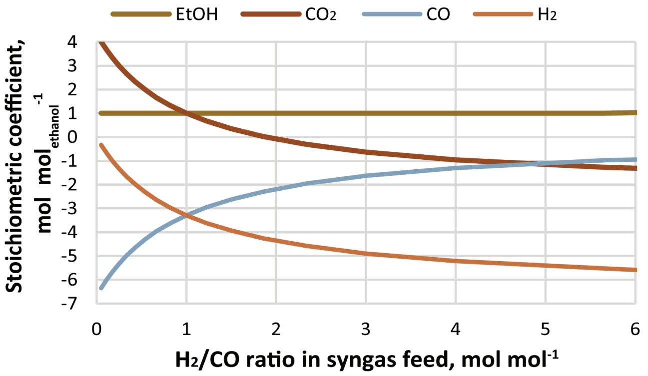


Figure 4. Stoichiometric dependence of CO_2 consumption/production with respect to the H_2/CO ratio in the syngas input stream.

After the syngas fermentation and DSP, the purity obtained is 99.6, 97.9, and 99.9 wt.% for ethanol, 2,3-butanediol and hexanoic acid, respectively; with a product loss, after gasification, of 5.6, 0.1 and 4.1%, respectively. The highest overall mass yield of whole supply chain was obtained for 2,3-butanediol from pine wood, which is 13 % higher than for ethanol production and 33% higher than for hexanoic acid production when the same feedstock is used. An advantage of using pine wood at the fixed steam to biomass ratio and gasification temperature, is that it produces the most elementary and molecularly compatible syngas for the three final products. In other words, the CO_2 consumption for products synthesis increases with higher H_2/CO ratios fed to the fermenter as shown in Figure 4. This higher consumption of CO_2 concentrated the CO and H_2 in the bioreactors, improving the mass transfer capacity and reducing further the requirements for CO_2 removal before syngas recycling. Nevertheless, since syngas composition is strongly influenced by gasification conditions,[38] optimal combinations of temperature and steam to biomass ratio could be determined, in order to produce syngas with a composition

Table 5. Yields of biomass, syngas, and final products. And composition of the resulting syngas at a gasification temperature of 850°C.

Process feature	PW	SB	CS	EW
Syngas composition (vol. % $_{dry}$)				
H_2	60.9	57.0	55.4	56.5
CO	28.1	28.6	30.0	29.0
CO_2	9.9	13.1	13.0	13.2
N_2	1.0	1.2	1.5	1.2
CH_4 (ppm)	593.2	379	412	386
NH_3 (ppm)	12.4	12	13	12
H_2S (ppm)	160.6	189	822	0
H_2/CO molar ratio	2.2	2.0	1.8	1.9
LHV ($kJ\ kg^{-1}$)	5101	5451	5378	5446
Biomass Yield ($kg_{biomass\ dry}\ kg_{biomass\ wet}^{-1}$) [a]	0.59 (NL), 0.60 (US)	0.18 (NL), 0.18 (BR)	0.81 (NL), 0.83 (US)	0.59 (NL), 0.77 (BR)
Syngas Yield ($kg_{syngas}\ kg_{biomass\ dry}^{-1}$)	1.20	1.14	1.18	1.19
Yield to product from biomass				
$kg_{ethanol}\ kg_{biomass\ dry}^{-1}$	0.43	0.38	0.37	0.38
$kg_{2,3\text{-}butanediol}\ kg_{biomass\ dry}^{-1}$	0.49	0.41	0.41	0.42
$kg_{hexanoic\ acid}\ kg_{biomass\ dry}^{-1}$	0.36	0.32	0.31	0.32

[a] Locations in brackets indicate the place where biomass is converted into syngas.

optimized to the type of fermentation product wanted, from a defined available feedstock. However, this analysis has not been performed in this study.

Economic evaluation

Results of the economic evaluation are discussed considering two main processing stages: (i) biomass supply and gasification to syngas, and (ii) bulk chemicals production via syngas fermentation and subsequent DSP. The direct comparison between the obtained MSPs and the available data for selling prices in the global market was considered as indicator to determine potential economic feasibility of the products. Additionally, the ethanol production costs are used to draw comparisons against data reported in literature for ethanol, produced from lignocellulosic biomass through different platforms: (i) the thermochemical pathway (i.e., gasification and FTS) and (ii) the biochemical route (i.e., pre-treatment, hydrolysis, and fermentation).

Table 6 shows the costs contribution for syngas production from the four feedstocks with their respective region of origin and according to the location for biomass gasification.

Table 6. Total production costs of syngas: contribution analysis by feedstocks and location.

Cost item	PW (US)		SB (BR)		CS (US)		EW (BR)	
	(NL case)[a]	(Local case)[b]	(NL case)[a]	(Local case)[b]	(NL case)[a]	(Local case)[b]	(NL case)[a]	(Local case)[b]
Costs contribution ($ ton$_{syngas}{}^{-1}$)								
Biomass production	15.0	24.6	18.3	33.6	32.5	38.5	34.4	56.3
Sizing	0.7	0.8	0.2	0.4	0.7	0.6	1.3	1.5
Drying	15.4	—	19.0	—	5.4	—	14.4	—
Densification	1.6	—	3.2	—	1.7	—	3.1	—
Truck transport	32.8	53.6	8.9	16.4	13.0	15.4	11.6	19.0
Train transport	12.4	—	4.2	—	43.8	—	—	—
Ship transport	18.3	—	38.7	—	18.6	—	37.1	—
Catalyst	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Utilities (see below)	43.3	21.7	48.5	32.7	45.2	23.1	43.5	28.5
Waste treatment	4.6	2.4	8.3	6.3	6.8	4.0	4.7	3.4
Depreciation	8.0	8.6	8.5	9.2	8.2	8.6	8.1	8.7
Maintenance	7.4	8.0	7.8	8.5	7.6	8.0	7.5	8.1
Insurance & local taxes	3.5	3.8	3.8	4.1	3.6	3.8	3.6	2.7
Labor	11.4	8.7	11.9	7.8	13.1	7.1	11.8	9.0
Laboratory charges	16.3	12.4	16.9	11.1	18.7	10.2	16.9	12.8
Total production costs	190.7	144.5	198.2	130.0	218.7	119.3	198.0	150.0
Contribution of utility costs ($ ton$_{syngas}{}^{-1}$)								
Electricity	0	1.9	0	4.2	0	1.4	0	3.6
Steam	26.3	9.4	27.9	13.6	26.9	9.6	26.8	13.0
Cooling water	12.4	7.9	12.2	8.7	11.5	8.2	12.0	8.5
Solid waste treatment	0.3	0.1	4.3	3.2	2.9	2.2	1.6	1.2
CO_2 removal	4.2	2.3	3.8	3.1	3.8	1.7	2.9	2.1
WWT	0.2	0	0.2	0	0.1	0	0.2	0
Total utility costs	43.4	21.6	48.4	32.8	45.2	23.1	43.5	28.4

[a] NL case: syngas production takes place in NL
[b] Local case: syngas production takes place in the region where the feedstock is produced

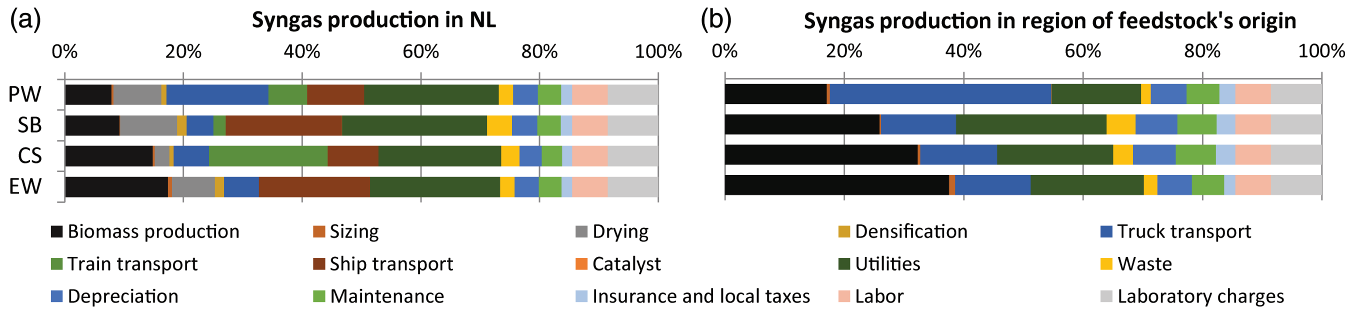


Figure 5. Cost contribution (in %) of syngas production for: (a) syngas production in NL, and (b) syngas production at the same region where feedstock is produced.

When syngas production takes place in the region of the feedstocks origin, the lowest production costs are obtained for CS in the USA. However, when syngas production takes place in NL after biomass import, the lowest syngas production costs among all feedstocks are obtained when PW from the USA is used. For the biomass import cases (Fig. 5(a)), the biomass supply costs represent the largest share of the total syngas production costs; i.e., around 50% (accounting for biomass production, sizing, drying, densification, truck transport, train transport, and ship transport). The relative contribution of the biomass supply to the total costs is larger when biomass gasification takes place in the same region of the feedstocks production (see local cases in Fig. 5(b)). For instance, when syngas is produced in the US, the biomass supply costs represent 55% for PW and 45% for CS, while in BR this contribution is 38% for SB and 51% for EW. Utilities are the second largest contributor to the syngas production costs (Fig. 5(a) and 5(b); they account for 20–25% of the total costs.

The second part of the production costs is related to the syngas fermentation into bulk chemicals and their further DSP. For the four feedstocks considered, the syngas production is the largest contribution to the total OPEX followed by the facility dependent costs which are related to the capital expenditures. Results are illustrated in Figs 6 and 7; syngas contribution to OPEX is in average 39, 29, and 34%, for ethanol, 2,3-butanediol and hexanoic acid, respectively (see Fig. 6(b) for 'raw materials' in combination with Fig. 6(c) for 'syngas'), while the facility dependent costs are 30, 32, and 30 %, respectively (Fig. 6(b)). The rest of the OPEX contribution comes mainly from the pH controlling substances, nutrients, and make-up solvents. All the process water required in the chemical production phase originates from the gasification process and is recovered from the syngas cooling; thus, no external process water is required.

The total production costs are obtained by adding up the contributions from biomass supply, syngas production, syngas fermentation and DSP. The lowest production costs were obtained for PW with production in the USA, while the ethanol turned out to be the least costly chemical to produce, followed by 2,3-butanediol and lastly, by hexanoic acid (Fig. 7(a)).

In general, the syngas fermentation gives the largest contribution to the production costs for the three products: 50–63%, 41–52%, and 44–53%, for ethanol, 2,3-butanediol and hexanoic acid, respectively (Fig. 7(a)). The main reason for this significant contribution is the large requirements of equipment and energy to overcome the low CO and H_2 mass transfer capacities in the bioreactors, which results in large fermentation volumes and power input for gas compression. In the case of hexanoic acid, the combination of the chain elongation unit (second fermentation step) with the DSP, represent only a minor part of the total production costs, due to the significantly lower fermentation volumes (no mass transfer limitation) and the relatively easier operations proposed for purification. The cost contribution of the DSP for ethanol production is relatively low because most of the product concentration is achieved within the fermentation stage, as ethanol is stripped out of the broth by the excess of syngas (Downstream processing section). Finally, although the recovery efficiency and conversion yield for 2,3-butanediol production are the highest among the three products compared, its DSP is the most resource intensive due to the limited concentration achieved within the fermentation. The 2,3-butanediol production process has also the highest CAPEX (Fig. 7(b)), which is mainly the due to the presence of the reverse osmosis unit (Fig. 3(b)) needed for partial broth dehydration.

The total production costs of ethanol here obtained are compared to those reported in literature for similar hybrid processes, i.e., the sugar platform (with biochemical pretreatment) and Fischer-Tropsch (after biomass gasification) as shown in Figure 8. Reported data show a substantial variation depending on considered process configurations

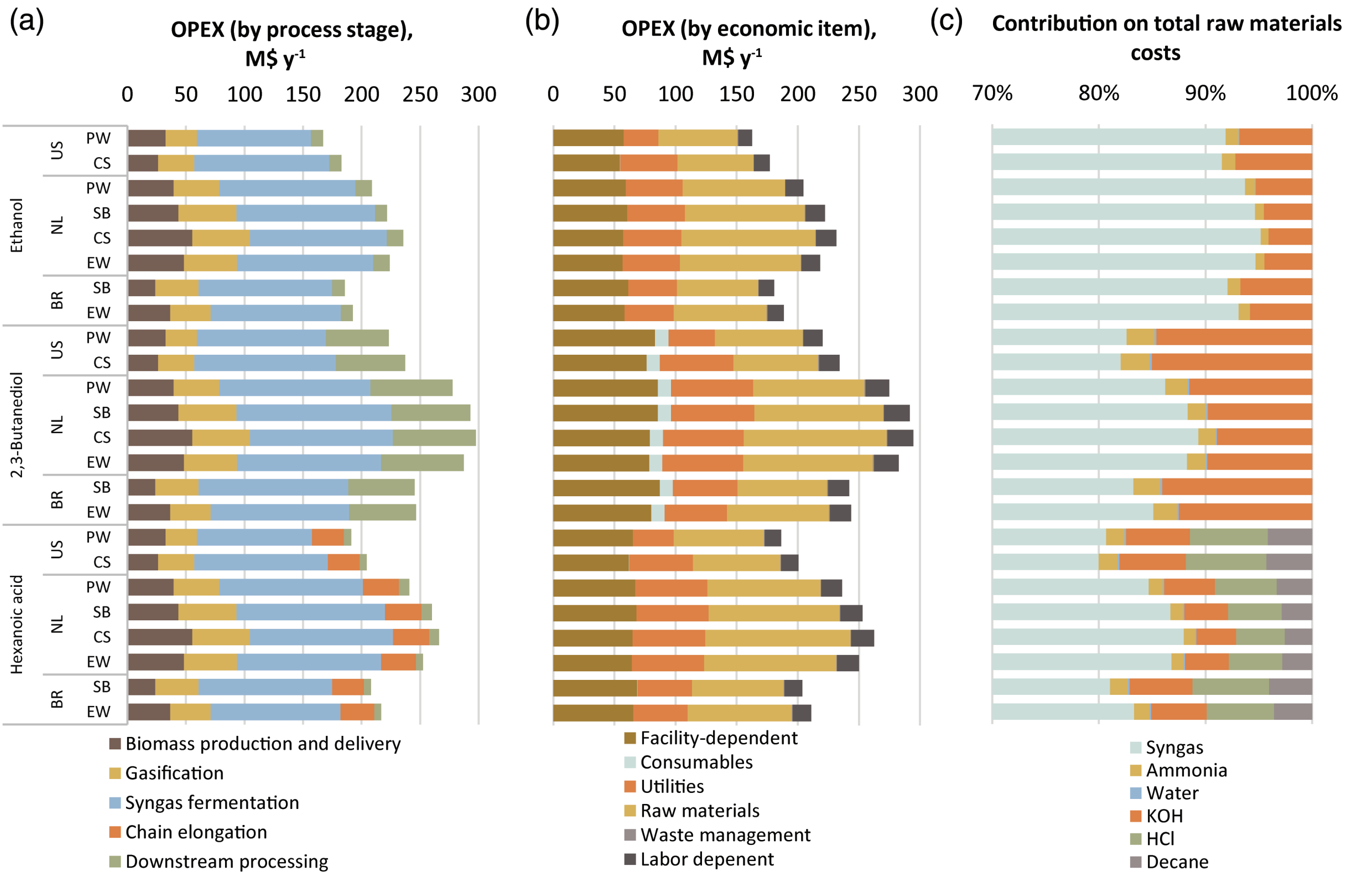


Figure 6. Break-down of operational costs for bulk chemicals production in all scenarios via the hybrid process. (a) Composition of OPEX by process stage, (b) composition of OPEX by major economic item, and (c) cost contribution of raw materials.

and assumptions. In general, most data show that the hybrid conversion route is the least cost-competitive option for ethanol production from lignocellulosic biomass. Thus, process optimizations are still required within this production pathway.

The MSP results for each case are shown in Figure 9. The lowest values, independently from the final product, are obtained when production takes place in the US from PW. The main reason for his result is the fact that the US has relatively low values for: electricity costs, interest rate on loans, location factor, tax on revenue, fuel prices, and biomass production costs. On the contrary, BR is the least attractive case (even considering that it has the lowest production costs of syngas) due to its highest values for electricity price and interest rates on loans.

The obtained MSP for ethanol are higher than the selling prices observed in the international market during the last ten years (Nasdaq Inc. (www.nasdaq.com)) (Fig. 9), meaning that the designed production chains cannot compete with commercially available routes for ethanol production. Due to limited access to international market prices for 2,3-butanediol, the MSP obtained for this product are compared to those reported for 1,4-butanediol;[109] the MSP fit within the price range reported for 1,4-butanediol (Fig. 9), making this 2,3-butanediol a potentially attractive product of the syngas fermentation platform. The MSP of hexanoic acid are compared to two types of products (Fig. 9): jet fuel and food-grade hexanoic acid. It is stated that hexanoic acid can be used as precursor of biofuels[110] and other products such as polymers, dyes or esters which require high purity of the acid.[111] The MSP for the acid are significantly higher than market prices observed for both fossil and bio-based jet fuel, however they are comparable (or lower) than those reported for food-grade hexanoic acid. However, there is a large difference between the global market size of both applications (i.e., as fuel or as high-quality feedstock); a discussion on the influence of production scale of hexanoic acid with respect to the MSP is included in the section Hexanoic acid production capacity.

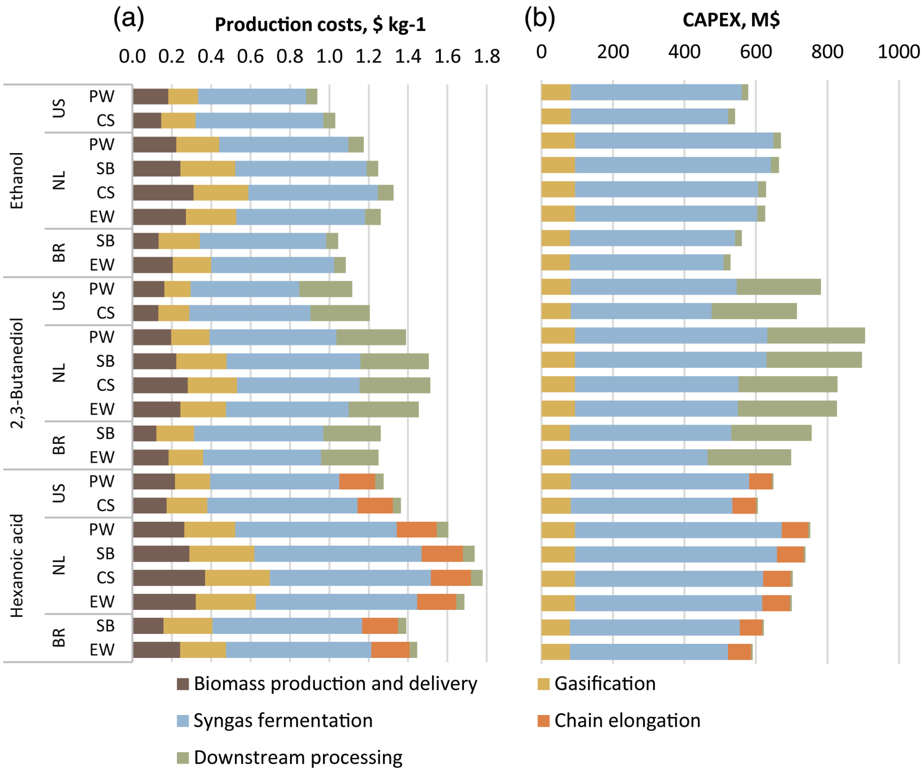


Figure 7. Break-down of total production costs and CAPEX by process stage. (a) Production costs, and (b) CAPEX.

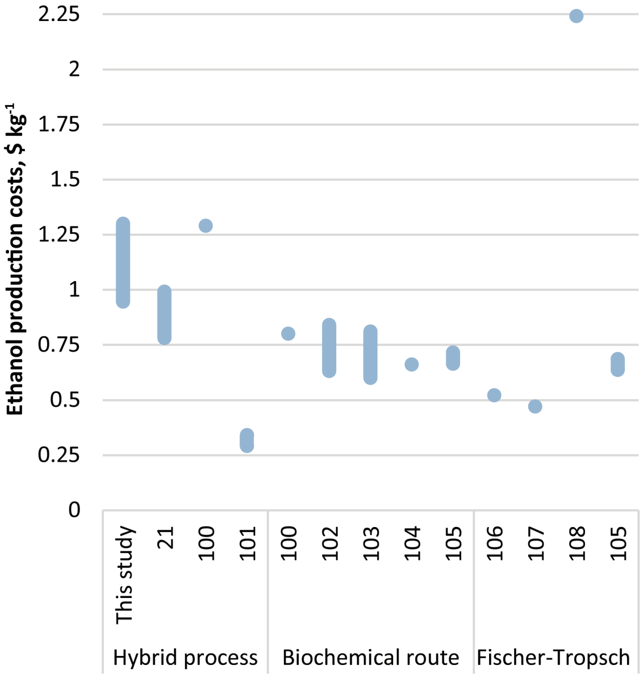


Figure 8. Comparison of total production costs for lignocellulosic ethanol by different platforms. Dots show punctual numbers, while lines show ranges. Numbers on the x-axis denote the respective literature reference.

Life cycle assessment

For a better understanding of the composition of the environmental impacts, the contribution from biomass production up to syngas production is discussed in first instance, and then the impacts analysis is done for the entire production chain.

The obtained environmental impacts (GWP and NREU) for syngas production in the three locations (NL, BR, and US) from PW, SB, CS, and EW are shown in Table 7. Eucalyptus usage in BR and NL and pine usage in the US lead to the lowest GWP, while sugarcane bagasse in BR leads to the lowest NREU. Corn stover has the highest environmental impacts for GWP, both in NL and the US. The worst NREU results are for PW and EW in NL. With respect to the geographical location, BR leads in general to the lowest impacts, while NL produces the highest impacts due mainly to additional impacts from international transport. Figure 10 shows a contribution analysis for GWP and NREU; two key factors contributing to the environmental impacts of syngas production are: steam consumption for gasification and biomass production. The contribution of the latter is larger since it includes biomass conditioning and delivery.

The environmental impacts, and their contributions from the process inputs for the entire supply chain and for each product are shown in Figure 11. The main contributor is electricity consumption, followed by syngas production and heat requirements. This tendency is consistent in all scenarios, however, the impacts from electricity are lower in BR compared to those in the US and NL.

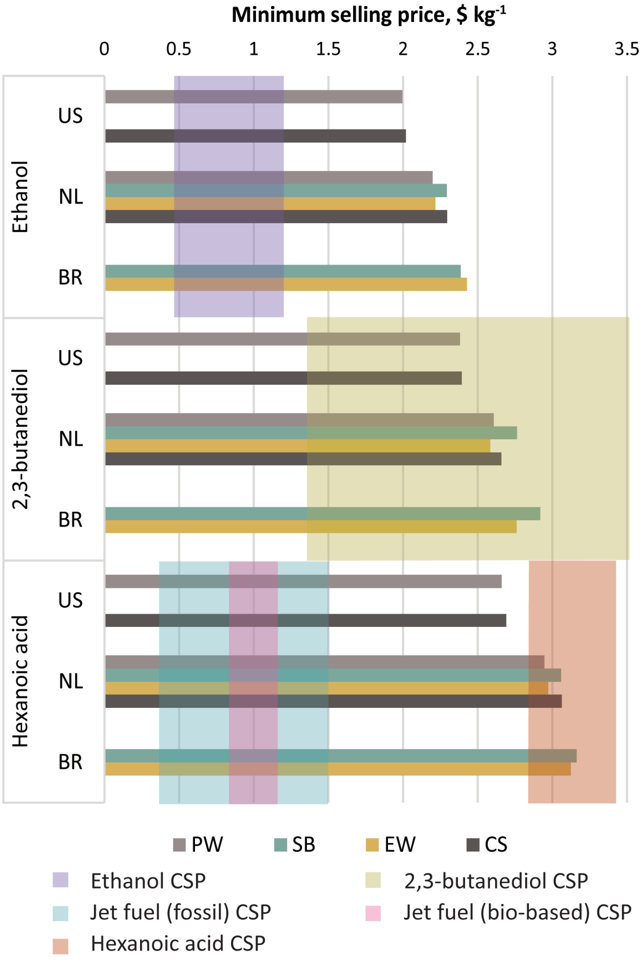


Figure 9. MSP for all products considering different locations for biomass production and gasification. Vertical colored rectangles represent the range of commercial selling prices for: ethanol (in violet), 1,4-butanediol (as equivalent to 2,3-butanediol, in golden), fossil jet fuel (in green), bio-based jet fuel [112] (in pink), and bio-based hexanoic acid(in red). CSP: commercial selling price.

Figure 12 compares the environmental performance of chemicals produced by the hybrid process against alternative production methods by considering other technologies and/or other feedstocks. In the cases of 2,3-butanediol and hexanoic acid, equivalent products were included as benchmark assuming that the syngas based products can act as potential replacement of these products. Ethanol produced from lignocellulosic biomass via the hybrid process generally shows higher environmental impacts (both NREU and GWP, 100 and 85 % higher) when compared to ethanol derived from first-generation and second-generation resources (Figs 12(a) and 12(d)). Furthermore, the usage of lignocellulosic materials (e.g. wood in the European Union (EU) and maize straw in the US) can lead to 45 % lower impacts than those for first-generation raw materials (e.g. wheat and sugarcane). Finally, when compared with gasoline, ethanol through the hybrid process could generate up to 48 and 64 % lower environmental impacts than the fossil fuel, in terms of NREU and GWP.

Production of 2,3-butanediol via the hybrid process resulted in a better environmental performance in comparison to 1,4-butanediol and 1,3-propanediol (both from fossil and bio-based feedstocks; Figs 12(b) and 12(e)). The GHG emissions obtained for the hybrid process show a potential reduction as high as 76 and 93% in GWP and NREU from values reported for the two other fossil-based diols. In the case of hexanoic acid, this product exhibits a similar performance as the one reported for fatty acids derived from vegetable oils, and until 80 % lower GWP for adipic acid (a six-carbon-chain dicarboxylic acid in whose production, large amounts of N_2O are released) (Figs 12(c) and 12(f)). Although the obtained results for 2,3-butanediol and hexanoic acid are in general encouraging for further process development, these results

Table 7. Environmental impacts (GWP and NREU) of syngas production.

Environmental impact category	Units	NL				BR		US	
		PW	SB	CS	EW	SB	EW	PW	CS
GWP	($kg_{CO2\text{-}eq}$ kg_{syngas}^{-1})	0.26	0.26	0.32	0.21	0.23	0.20	0.21	0.29
	($kg_{CO2\text{-}eq}$ MJ_{syngas}^{-1}) [a]	0.051	0.047	0.059	0.038	0.042	0.036	0.041	0.053
NREU	(MJ kg_{syngas}^{-1})	5.87	3.71	5.20	5.99	3.13	3.74	3.46	4.09
	(MJ MJ_{syngas}^{-1}) [a]	1.15	0.68	0.97	1.10	0.57	0.69	0.68	0.76

[a] LHVs are calculated based on the resulting syngas composition from each feedstock as shown in Table 5.

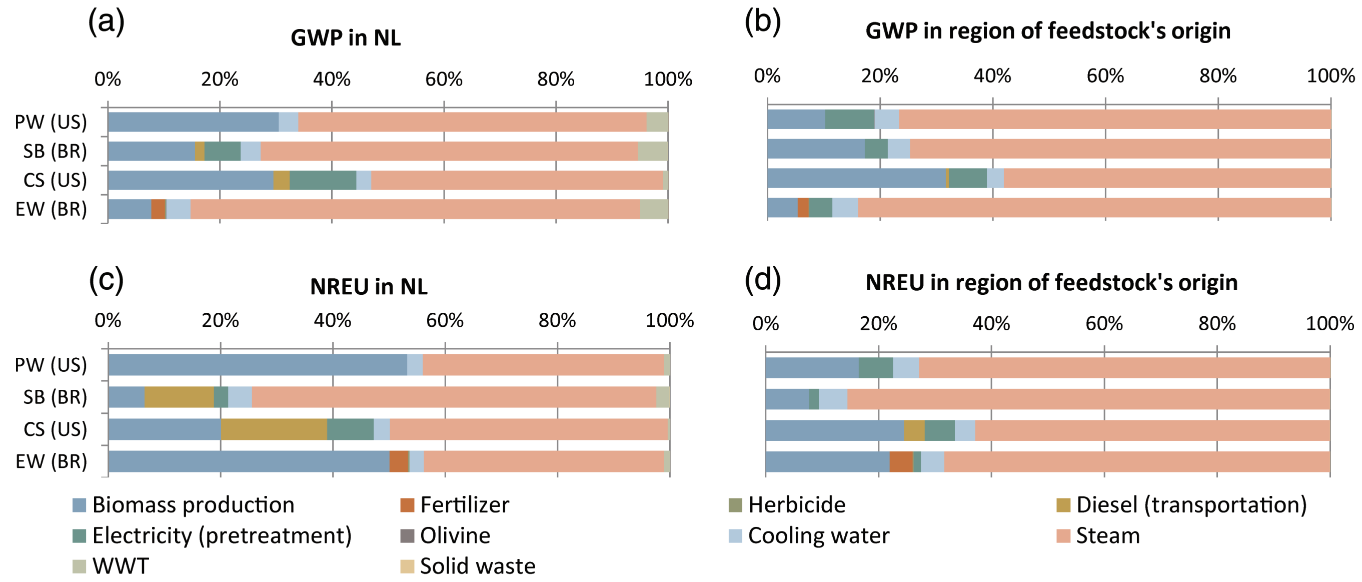


Figure 10. Contribution analysis for environmental impacts of syngas production: (a) GWP in NL, (b) GWP in the region of feedstocks origin, (c) NREU in NL, (d) NREU in the region of feedstocks origin

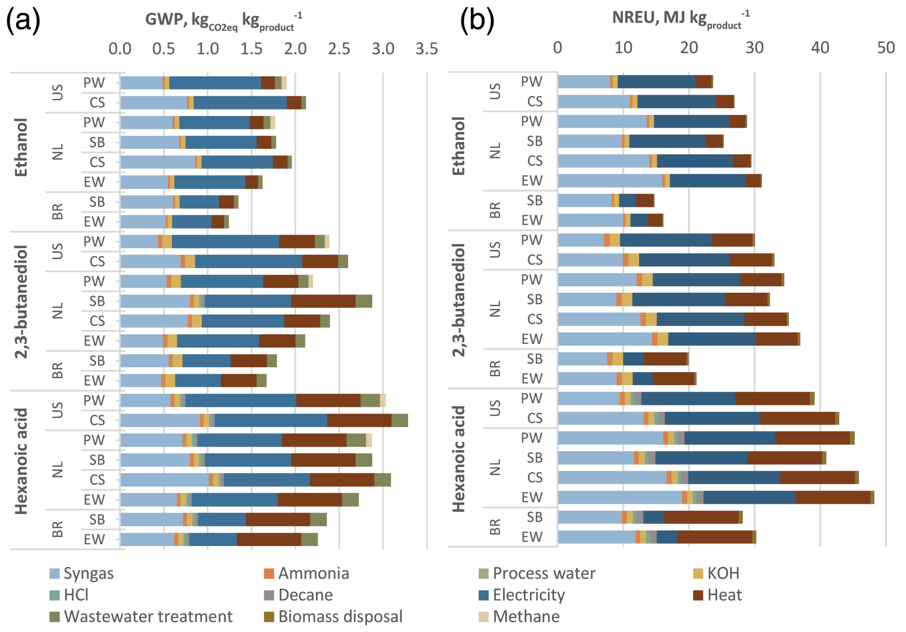
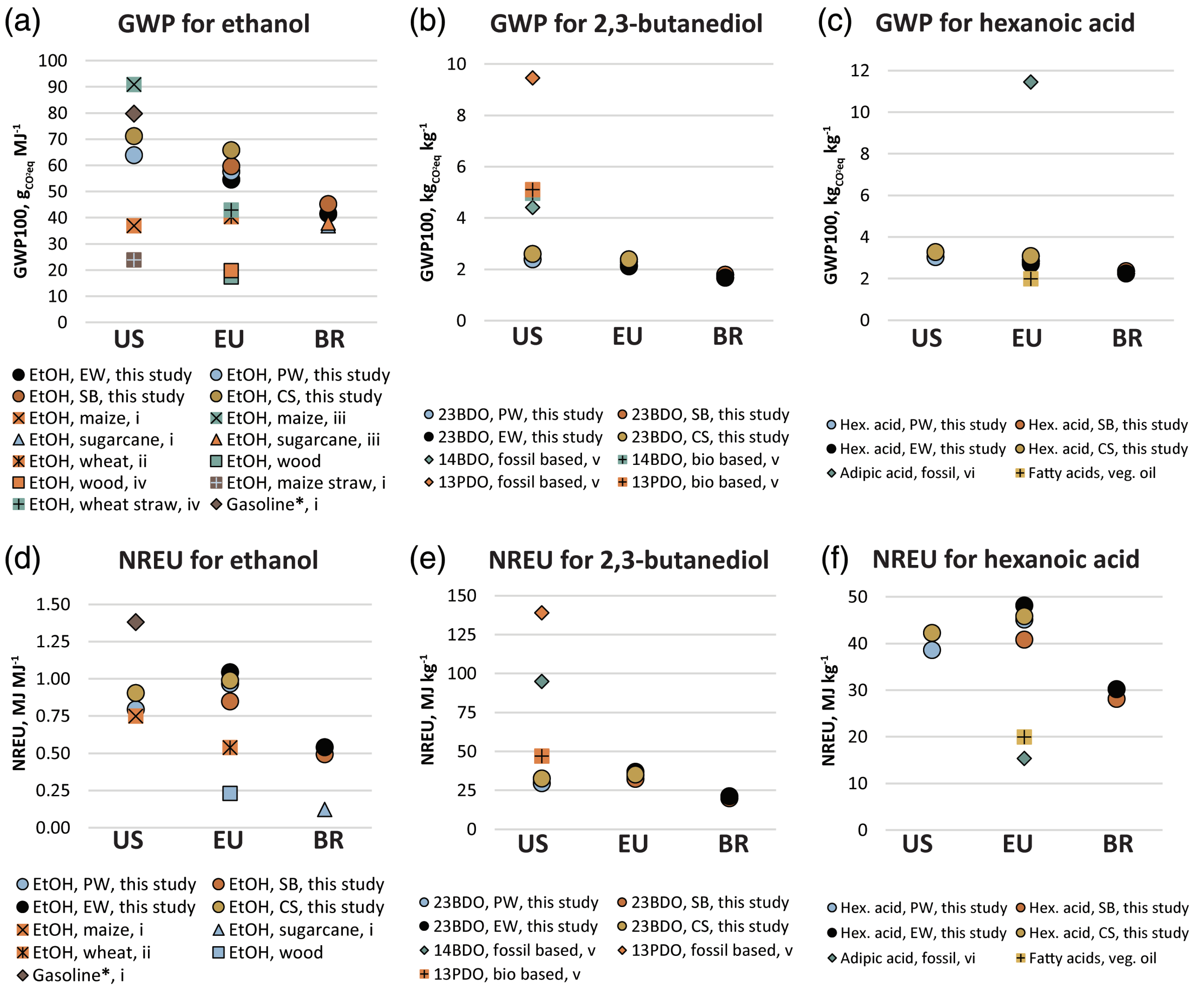


Figure 11. Environmental impacts of the supply chain for bulk chemicals production in the US from PW via the hybrid process. (a) GWP and (b) NREU.

should also be prudently considered for future research. given the lack of environmental impacts reported in literature on producing these two products through other pathways.

Although the three products of the hybrid process could potentially lead to significant reductions in GHG emissions and NREU when compared to their fossil-based counterparts, the economic performance of ethanol and hexanoic acid will not be promising if current oil and its products' prices are maintained and more optimized processes are not designed. However, 2,3-butanediol could become a key product as it has shown a competitive performance with its bio- and fossil-based equivalents.



* Gasoline is fossil-based and its impacts include CO_2 emissions from final combustion.

Figure 12. Environmental impacts of the hybrid process-based products and comparison with data reported in literature for different routes. GWP of: (a) ethanol, (b) 2,3-butanediol, (c) hexanoic acid; and NREU of (d) ethanol, (e) 2,3-butanediol, (f) hexanoic acid. List of references: i: [113]; ii: [114]; iii: [115]; iv: [116]; v: [117]; vi: [118]. Second-generation feedstocks considered in ethanol production follow the pathway with bio-chemical pre-treatment of cellulose.

Sensitivity analysis

The analyses shown in the previous sections are considered here as the base cases; these are used as reference points for the sensitivity analysis now discussed.

Gasification temperature

The gasification temperature for all feedstocks was varied between 650 and 1050°C to analyze its impact on the resulting syngas composition. The changes in the syngas composition showed a similar trend in all cases. Results are exemplified using only the data for pine wood gasification (Figure 13). Higher gasification temperatures led to higher concentrations of H_2 and CO, thus favoring the

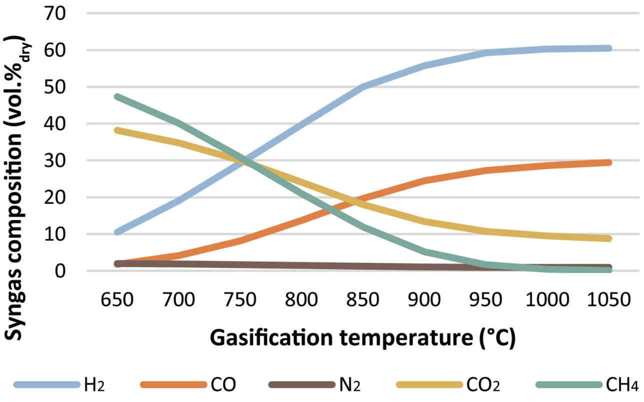


Figure 13. Influence of gasification temperature on the raw syngas composition for pine wood.

Table 8. Optimal gasification temperature for each feedstock and accompanied syngas compositions in vol.%.

Optimal gasification condition	Feedstock			
	PW	SB	CS	EW
Temperature (C°)	1000	950	850	900
Composition (vol.% $_{dry}$)				
H_2	60.3	55.6	43.8	52.1
CO	28.6	28.3	22.5	25.8
N_2	1.0	0.0014	0.002	1.3
CO_2	9.5	14.9	22.9	16.6
CH_4	0.47	1.1	9.9	3.9
H_2S	0.017	0.021	0.1	0
NH_3	0.077	0.12	0.86	0.28
H_2/CO ratio	2.1	2.0	2.0	2.0

subsequent syngas fermentation in terms of mass yields and lower CO and H_2 dilution. Furthermore, the optimal gasification temperature is considered here as the one that produces minimum amounts of CH_4 and CO_2 (<10%), while keeping the H_2/CO ratio around 2. Hence, the optimal gasification temperature for all feedstocks was determined as shown in Table 8.

Tar reformer

Considering that the tar reformer represents 25% of the purchase equipment cost for the gasification plant and that this unit may be removed when gasification is done at the optimal temperature (previous section), its exclusion could help to reduce the overall production costs; however, the final viability of this decision will depend on the effects on the syngas composition and its suitability for fermentation. In the case of PW, the syngas production costs are reduced by 20%. Positive effects are also obtained for the environmental performance: GWP and NREU are reduced by 14% and 16%, respectively, as shown in Table 9. Unfortunately, the resulting ammonium concentration with tar reformer exclusion (770 ppm, Table 10) is much higher than the value reported as tolerable for fermentation, 40 ppm.[119,120]

Although the resulting syngas is not fully free of impurities for fermentation, results suggest that a higher microbial tolerance of contaminants would significantly improve the overall economic and environmental performance of the process.

Table 9. Effects of exclusion of the tar reformer on the syngas flow, composition, production costs and environmental impacts. Results presented for gasification of PW at 850°C with tar reformer vs. gasification of PW at 1000°C (optimal temperature) excluding tar reforming.

Gasification variable	Gasification at 850 °C with tar reformer	Gasification at 1000 °C and exclusion of the tar reformer
Flow rate (kg s^{-1})	13.95	17.7
Composition (vol.% $_{dry}$)		
H_2	60.9	60.3
CO	28.1	28.6
CO_2	9.9	9.5
N_2	1.0	1.0
CH_4 (ppm)	593.2	500
NH_3 (ppm)	12.4	770
H_2S (ppm)	160.6	170
H_2:CO ratio	2.1	2.1
LHV (kJ kg^{-1})	5101	6553
Production cost ($ ton_{syngas}^{-1})	144.50	115.45
Environmental impacts		
GWP ($kg_{CO2\text{-}eq}$ kg_{syngas}^{-1})	0.21	0.18
NREU (MJ kg_{syngas}^{-1})	3.46	2.90

Heat recovery in the syngas production phase

The heat drawn from syngas during its final cooling (unit H108 in Fig. 2) was considered to be a useful source of energy, thus two potential uses for the heat recovered were analyzed: generation of electricity or steam.

When electricity is generated and used within the process, the syngas production costs significantly increase (16–19% for NL, 21–31% for BR, and 35–45% for the US) as shown in Table 10. This increase is due to the low thermal efficiency of the steam turbine and additional equipment costs; not enough electricity is generated to compensate for the additional overall costs. On the other hand, the environmental impacts are reduced by 13–26% and 12–20 % for GWP and NREU, respectively.

When steam is internally produced, a slightly larger reduction in the environmental impacts is achieved (19–31% for GWP and 19–23 % for NREU), while the syngas production costs are significantly reduced (22–29%) as shown in Table 10. The largest influence of steam generation on the economic and environmental performances

Table 10. Economic and environmental performances for the base cases and the two strategies for heat recovery in the syngas production phase: (i) electricity production and (ii) steam generation.

Cases	NL				BR		US	
	PW	SB	CS	EW	SB	EW	PW	CS
Base cases								
Production cost (\$ ton^{-1})	190.73	198.21	218.72	197.96	129.98	150.00	144.50	119.27
GWP (kg$_{CO2\text{-}eq}$ kg^{-1})	0.26	0.26	0.32	0.21	0.23	0.20	0.21	0.29
NREU (MJ kg^{-1})	5.87	3.71	5.20	5.99	3.13	3.74	3.46	4.09
Electricity production								
Yield (MJ kg$_{syngas}$$^{-1}$)	0.92	0.84	0.85	0.84	0.84	0.84	0.92	0.85
Production cost (\$ ton^{-1})	221.49	237.20	254.97	233.52	169.80	181.79	194.84	172.65
GWP (kg$_{CO2\text{-}eq}$ kg^{-1})	0.22	0.20	0.28	0.18	0.17	0.16	0.18	0.25
NREU (MJ kg^{-1})	5.08	3.21	4.60	5.27	2.51	3.10	3.01	3.56
Steam production								
Yield (kg kg$_{syngas}$$^{-1}$)	1.21	1.10	1.11	1.10	1.10	1.10	1.21	1.11
Production cost (\$ ton^{-1})	134.98	150.92	170.24	149.42	123.76	140.80	144.14	120.96
GWP (kg $_{CO2\text{-}eq}$ kg^{-1})	0.20	0.18	0.26	0.16	0.17	0.16	0.18	0.24
NREU (MJ kg^{-1})	4.51	2.89	4.17	4.74	2.54	3.13	2.95	3.47

occurs when syngas production takes place in NL, this is because steam is the second largest contributor to the production costs after feedstocks.

Gas flow rate across fermentors and product concentration

The influence of gas flow rate across the syngas fermentors and product concentration are studied only for ethanol and 2,3-butanediol, since (i) these two are the only direct products of syngas fermentation, and (ii) hexanoic acid is assumed to be produced at saturation concentration during chain elongation. At first, syngas fermentations were modeled considering the ethanol and 2,3-butanediol concentrations of 10 and 33 g L^{-1}, respectively, with corresponding to the maximal gas flow rates of 5565 and 5413 mol s^{-1} (Fig. 14(b)). Lower gas flow rates proved to reduce the mass transfer capacity as well as the volumetric production capacity, resulting in a larger number of reactors to maintain the same throughput. However, at the highest gas flow rates (in which gas hold-up in the bioreactors is around 15%), compressors require more energy and larger capacities. Thus, a reduction in the gas flow rate from the highest to the lowest value would increase of the MSP of ethanol and 2,3-butanediol by 140 and 103%, respectively (Fig. 14(a)). Furthermore, in the case of ethanol, its concentration in the fermentor depends on the gas flow rate due its removal by stripping. Thus, lower gas flow rates result in higher concentrations, and as a consequence in higher MSP (Fig. 14(b)) due to the extra fermentation volume required. In the case of 2,3-butanediol, which is removed along with the broth, a five-fold increase in concentration would lead to a significant size reduction, and therefore a reduction in equipment investment, especially in the reverse osmosis unit. This investment decrease would lead to a MPS reduction of 21% as shown in Figure 14(b). However, further concentration increments beyond 30 g L^{-1} would only have minor economic benefits, given the asymptotic trend of the MSP function observed in Figure 14(b).

The GWP performance of both products showed to be proportional to gas flow rate (Fig. 14(c)) due to direct relation between the gas flow rate and the electricity consumption in the compressors. These relative potential reductions in environmental impacts were similar for both products. For ethanol, however, at even the lowest gas flow rate, the GWP is still 125% higher than that reported for first-generation bioethanol produced in BR from sugarcane.[113] When the concentration is varied instead, the impacts related to ethanol production follow and inverse relation as the one observed in Fig. 14(c); but for 2,3-butanediol the change is barely noticed, with a variation of 0.11% on its GWP (results not shown).

Interest rate and payback time

Figure 15(a) shows the effects of the interest rates on the MSP for ethanol production, where the middle points

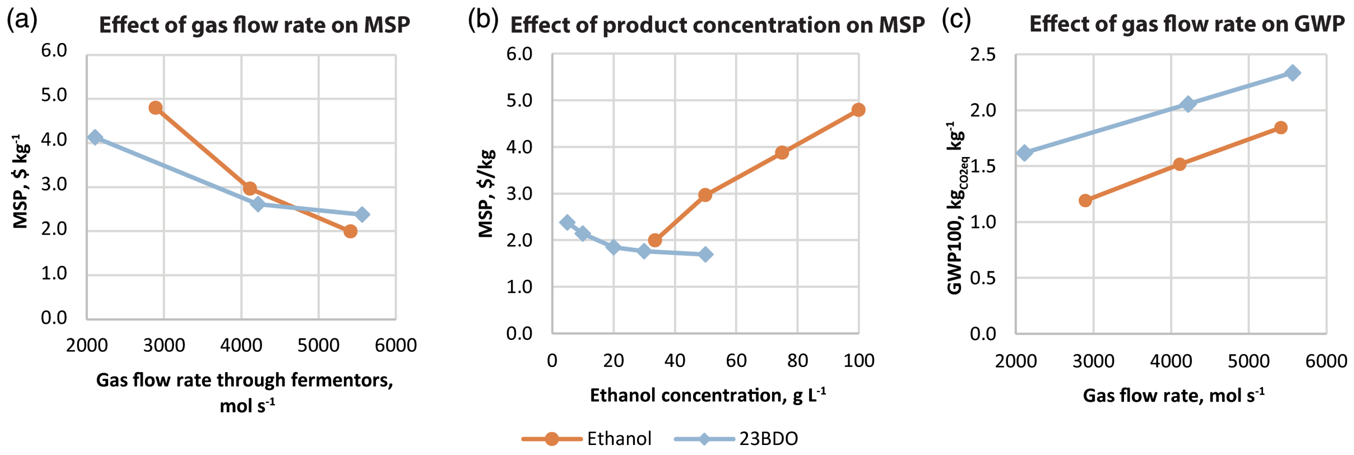


Figure 14. Influence of two syngas fermentation parameters on the economic and environmental performance of ethanol and2,3-butanediol production (from PW in the US): (a) effect of gas flow rate on MSP, (b) effect of ethanol concentration on MSP, and (c) effect of gas flow rate on GWP.

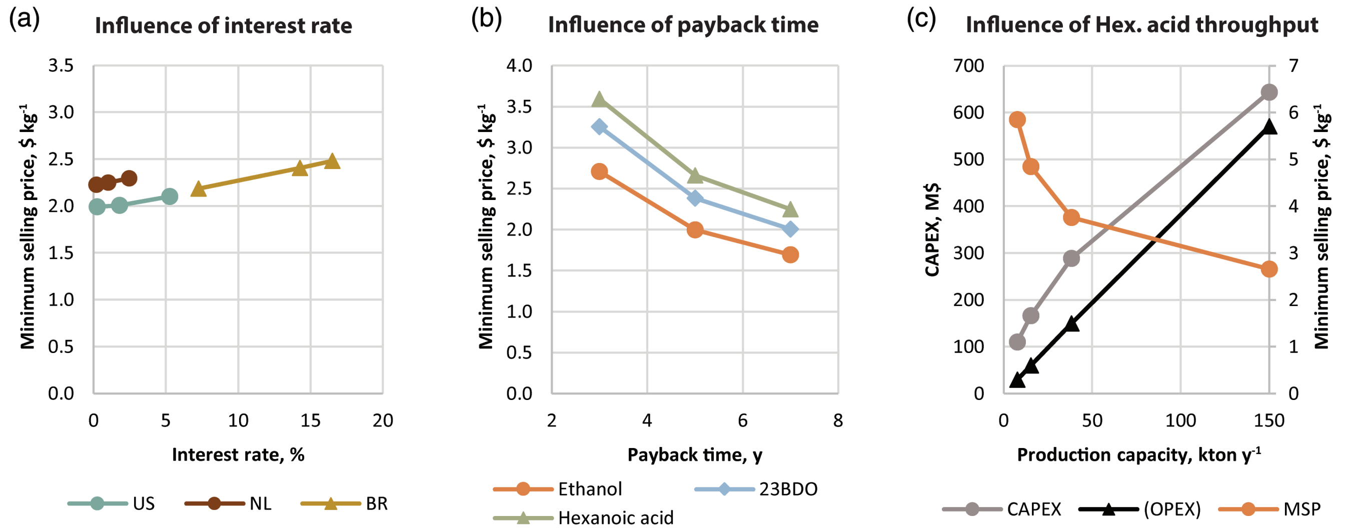


Figure 15. Sensitivity analysis. a) Influence of interest rate on MSP for ethanol production (US: 0.25–5.25%, NL: 0.20–2.45%; BR: 7.25–16.50%); (b) Influence of PBT on MSP; and (c) influence of hexanoic acid production capacity on CAPEX, OPEX and MSP (from 8 to 150 kton y^{-1}).

represent the cases discussed in the Economic evaluation section. Decrease of the interest rates would only result in minor reductions on the ethanol MSP: 7.4, 3.2 and 13.5% for the US, NL, and BR, respectively. Thus, the US is the best geographical option (even at the highest interest rate). BR could become an interesting place for production if the interest rates are on the low side of the last ten years tendency; however, this country has the highest uncertainty of the three locations analyzed which may represent a risk to possible investments.

The effects of the PBT on the MSP (Figure 15(b)) are significantly larger than those of the interest rates. In average, a MSP decrease of 38% is obtained when the PBT increases from 3 to 7 years. However, the pay-back time preferred by investors is generally between 3 and 5 years.[83,87]

Hexanoic acid production capacity

CAPEX and OPEX are known to be reduced when the production capacity increases due to the economy of scale. This is also the case for the MSP. However, in this case, two different production scales for hexanoic acid can be considered according to the expected application, already explained in the Economic evaluation section. The global market for the former fuel application would be able to absorb large production volumes (e.g. 150 kton y^{-1}) while the demand for the latter high-quality applications would only be able to handle small scale production before saturating the market (due to lack of published data, the market size for decanoic acid was considered as reference: 70 kton y^{-1}) (www.transparencymarketresearch.com). The MSP of hexanoic acid at large scale production is significantly higher than the commercial price of jet fuel (0.33–1.44 \$ kg^{-1}) in the international market (Fig. 15(c)). It is also higher than the MSP reported for biojet fuel production via hydrothermal liquefaction of PW, EW and from macauba oil.[112] Finally, for small scale production, the obtained MSP is comparable to the commercial price of food-grade hexanoic acid in the international market (2.8–3.4 \$ kg^{-1}) (Alibaba.com) only when the annual production is in the range of 50–75 kton which could already be at near saturation of the market. Hence, hexanoic acid is doubtfully an attractive product of the hybrid process.

Fermentor purchase cost

If the purchase cost of each syngas fermenter is lowered to the half of the value assumed, the MSP for ethanol and 2,3-butanediol are lowered by 18 and 13%, respectively (Supporting Information). On the case of hexanoic acid, if the chain elongation fermentor would cost the half, the product's MSP is lowered by 7%. On the other hand, if the purchase costs are doubled, the MSP of ethanol, 2,3-butanediol and hexanoic are raised by 36, 27, and 13%, respectively. From this analysis, two things became evident, (i) the existing large uncertainty on the economic performance of ethanol and butanediol, and (ii) the fact that the contribution of the fermentors purchase cost to ethanol specially, is much more determinant than for the two other products.

Conclusions

Results suggest that the syngas platform, through the hybrid process (biomass gasification followed by syngas fermentation), is a potentially competitive route to produce 2,3-butanediol. This platform showed also to perform slightly poorer, in both economic and environmental terms, than more developed second-generation technologies for ethanol production. In the case of 2,3-butanediol, the designed supply chain and process lead to better economic and environmental performances than those of the fossil and bio-based technologies reported for its equivalents 1,4-butanediol, and 1,3-propanediol. In fact, production of ethanol, 2,3-butanediol and hexanoic acid though the hybrid process may potentially lead to lower GHG emissions than their respective fossil-based counterparts. However, uncertainties still exist within the economic performance due to the lack of commercial-scale projects that could serve as reference for cost-related data.

In the hybrid process, the fermentation stage makes use of the low-cost syngas platform, compared to the expensive sugar-based platform, as carbon source. However large CAPEX and OPEX are still associated to the syngas fermentation (mainly due to low CO and H2 MTC and large power consumption by gas recycling) and DSP (in the case of 2,3- butanediol, due mainly to the low concentration of products). Yet, further improvements may be possible by increasing the gas–liquid mass transfer capacity inside the syngas fermenters or by process integration and optimization. Thus, heat recovery from the gasification stage showed to be beneficial from an environmental and economic point of view. In general terms, the application of the hybrid process has shown to be an interesting option to produce bulk chemicals that otherwise would require complex DSP to separate and purify the main product from the fermentation broth; that is the case of, for example, 2,3-butanediol.

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