

Production of 1,3-butadiene and ϵ -caprolactam from C6 sugars: Techno-economic analysis

Jonathan Moncada, Iris Vural Gursel, Ernst Worrell, Energy and Resources, Copernicus Institute of Sustainable Development, Utrecht University, The Netherlands

Andrea Ramírez, Energy and Resources, Copernicus Institute of Sustainable Development, Utrecht University, The Netherlands; Energy and Industry, Faculty of Technology, Policy and Management, Delft University of Technology, The Netherlands

Received November 13, 2017; revised January 21, 2018; accepted February 14, 2018

View online at March 22, 2018 Wiley Online Library (wileyonlinelibrary.com);

DOI: 10.1002/bbb.1876; *Biofuels, Bioprod. Bioref.* 12:600–623 (2018)

Abstract: This study assesses the techno-economic performance of production lines for obtaining 1,3-butadiene and ϵ -caprolactam from C6 sugars. Process models were developed to assess their technical performance and to derive inputs for economic analysis. The economic assessment was carried out using net present value (NPV) and production costs as indicators. Sensitivity analyses were carried out to account for the effects of variations in inputs, such as processing capacity, valorization of humins, and prices, on the economic outputs. Results indicate that both production lines perform similarly from an energy intensity point of view (34–50 MJ/kg of main product). However, in terms of yield (kg of product per kg C6 sugar), caprolactam shows higher values by a factor of 1.6–3.6 in comparison to that of butadiene. The butadiene production line is not economically attractive, showing a negative NPV (–647 to –642 M€) and production costs 3–5 times higher than the reference market price (Case I 4369 €/tonne, Case II 3406 €/tonne). The caprolactam production line seems to be unfeasible with negative NPV (–229 M€) and production costs 30% higher than the reference price (Case III 2595 €/tonne, Case IV 1875 €/tonne). However, if the production yield is increased, the caprolactam production line becomes economically attractive with production costs 6% lower than its reference market price. The production costs of caprolactam can be further decreased if the process capacity is increased, reflecting the benefits of the economies of scale, as well as including heat and power produced from humins. Overall, the caprolactam production line shows higher economic potential. © 2018 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: C6 sugars; butadiene; caprolactam; process modeling; techno-economic analysis.

Introduction

The biorefinery concept has emerged as an analogy to oil refineries, where instead of using oil, biomass is used as feedstock and refined into multiple streams with broad applications in industry.^{1,2} Multiple types of feedstock are used in biorefineries, including crops, lignocellulosic biomass, macroalgae and microalgae.^{2,3} These feedstocks have been used as potential precursors to obtain platforms (e.g., carbohydrates, vegetable oil, biogas, lignin), which are later converted into fuels, chemicals, and / or materials.^{4,5}

The carbohydrates platform stands out due to its unique versatility as a precursor for multiple valuable products with many applications.^{6–8} The carbohydrates platform, which generally consists of hexoses (e.g., C6 sugars), pentoses (e.g., C5 sugars), or disaccharides, has traditionally been produced from sugary crops such as corn, sugarcane, and sugar beets. Recently greater attention has been given to its production from lignocellulosic biomass such as agricultural residues (e.g., corn stover, wheat straw), grasses (e.g., switchgrass), and wood (e.g., softwood), among others. Independent of the source of the carbohydrates, many of the derivatives from the conversion can be used as chemical building blocks and can be produced via chemical catalysis, via bio-catalysis (e.g., fermentation) or by both pathways.⁶ Bozell and Petersen⁷ highlighted a top-ten list of possible derivatives from carbohydrates with high relevance for biorefineries. From that list, ethanol appeared as one of the most representative ones not only due to its application as fuel but also due to its use as a building block. Ethanol is a potential raw material for chemicals such as ethylene, propylene diethyl ether, and 1,3-butadiene.⁹ Bozell and Petersen⁷ also pointed out that levulinic acid is an important carbohydrate derivative due to its possible use as raw material for producing pyrrolidones, lactones, and levulinate esters. Bio-based levulinic acid may be produced directly from C6 sugars using the biofine process.^{10,11}

Among the different potential carbohydrate derivatives, 1,3-butadiene and ϵ -caprolactam appear to be of great interest as possible bio-based materials. Butadiene is an important chemical for the production of synthetic rubbers. About 70% of worldwide butadiene production is used for tire manufacturing. Butadiene has traditionally been produced in oil refineries as a by-product from steam cracking of naphtha, liquefied petroleum gas (LPG), ethane, propane, or butane to produce ethylene and other olefins.^{12,13} Alternatively, 1,3-butadiene can be produced from the catalytic conversion of ethanol.^{9,12–14}

Caprolactam is the feedstock for producing nylon-6, a well-known polymer and one of the most widely used nylons.¹⁵ Caprolactam is traditionally produced from benzene in a four-step process in which benzene is first converted into cyclohexane, and subsequently into cyclohexanone.^{15,16} The third step consists of the conversion of cyclohexanone into cyclohexanone oxime, which is finally converted into ϵ -caprolactam.^{15,16} As an alternative, the production of caprolactam can start from γ -valerolactone (GVL), which can be produced from bio-based levulinic acid (LA).¹⁵

Many authors have studied the reaction mechanisms, process conditions, yield and selectivity for producing butadiene from ethanol;^{17–19} however, literature is scarce on techno-economic assessments of butadiene production from carbohydrates. Early stage assessments (combining techno-economic and environmental indicators) of butadiene production from ethanol were carried out, concluding that it has benefits over naphtha-based butadiene.^{9,20} Nevertheless, the scope of these analyses did not include aspects such as capital investment and some operating costs as the case of utilities. Cespi *et al.*, (2016)²¹ made a multi-criteria assessment (including techno-economic and environmental indicators) of different processes of butadiene production from ethanol, concluding that one-step conversion performs better than a two-step method. The economic assessment in this study included operational costs such as raw materials and utilities, but excluded aspects such as capital investment. Recently, Farzad *et al.* (2017)²² carried out a more detailed techno-economic and environmental assessment of butadiene production from sugarcane bagasse (with ethanol as intermediate and co-product), concluding that there is a need for higher butadiene selling prices to make bio-based production economically attractive.

As in the case of butadiene, many authors have studied reaction mechanisms, conditions, yields, and selectivity of the steps for producing caprolactam from carbohydrates, including all intermediate routes. For instance, Girisuta and Heeres²³ reported a summary of yields, process conditions of several routes, and kinetic studies to produce levulinic acid. Other authors have reported yields and conditions of γ -valerolactone from levulinic acid^{24,25} and the production of caprolactam from γ -valerolactone.¹⁵ Literature on the techno-economic assessment of bio-based caprolactam production is scarce. Han²⁶ carried out a techno-economic assessment of caprolactam production starting from lignocellulosic biomass.

One common aspect of the studies on detailed techno-economic assessment of butadiene²² and caprolactam²⁶ is that the scope of the analysis starts directly from lig-

nocellulosic biomass. However, given the importance of the carbohydrate platform for the bio-based economy, it would be interesting to carry out the assessment starting from C6 sugars. This is important for countries where the availability of biomass is limited and where the C6 sugars trade may play a crucial role, for instance through imports of glucose syrup derived from corn for biorefineries. Considering the background discussed above, the scarcity of literature taking a systems analysis perspective of both butadiene and caprolactam production lines, and their potential for the bio-based chemical market to substitute chemicals that have traditionally been produced from oil sources, the aim of this study is to investigate the production lines for butadiene and caprolactam using C6 sugars as feedstocks from a techno-economic perspective, to identify bottlenecks in each production line, and to determine which is the most economically attractive. The analysis will follow an integrated biorefinery approach and will report on the effect of various process improvements, valorization of residues, processing scales, and economic parameters such as prices on overall performance.

Materials and methods

In this study a techno-economic analysis of the production of 1,3-butadiene and ϵ -caprolactam was conducted. The sequence of steps followed is summarized in Fig. 1. Details of methods used, data, and assumptions are provided below.

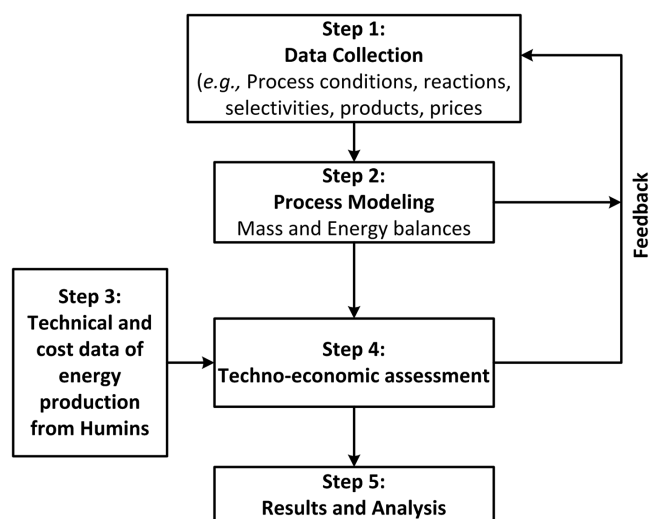


Figure 1. General description of the methodological approach for assessment of butadiene and caprolactam from C6 sugars.

Process modeling

To assess the technical performance, process models were developed in Aspen Plus v8.4 (Aspen Technology, Inc., Houston, USA). Several of the compounds involved in the modeling were not available in the databases of Aspen Properties, so a property database of the National Renewable Energy Laboratory was used, which is based on the work of Wooley and Putsche.²⁷ Furthermore, the nonrandom two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden O'Connell equation of state was used to describe the vapor phase. All processes are assumed to operate in continuous mode and whole-year operation (i.e., 8000 h/year). In all cases, energy integration was considered by using excess heat from available streams internally. Nevertheless, optimization using pinch analysis was not considered and the integration of the water stream and water recycling was not included.

Basis for design

This section focuses on the assumptions and data used to build the process models for both the butadiene and caprolactam processes. The processes were designed based on similar processes reported in the literature and in some cases following heuristics of typical chemical engineering conceptual design.

For both butadiene and caprolactam processes, C6 sugars are the main feedstock. In this study, the capacity of C6 sugars is set to 400 ktonne per year. This capacity was estimated roughly, based on the conversion of 1000 ktonne/year of dry lignocellulosic biomass, which is representative for large commercial operation of biorefineries.²⁸ In the base case, this flowrate was equally distributed to feed the production processes of butadiene and caprolactam (200 ktonne/year of C6 sugars feeding each process). The impact of this assumption is considered as part of the sensitivity analysis. The C6 sugar price (independently of whether it was produced from crops or lignocellulosic biomass) is fixed as an input for the economic analysis of both butadiene and caprolactam production (300 €/tonne,²⁸ typical range 200–400 €/tonne).

Figure 2 shows a simplified block diagram of the sequences considered in this study. Each block represents a production process. This is explained in more detail below. The block with a dashed border represents a combined heat and power unit in the case where humins are valorized. It is assumed that both heat and power produced in this step are distributed equally to both the butadiene and caprolactam lines. Surplus electricity (if any) is considered

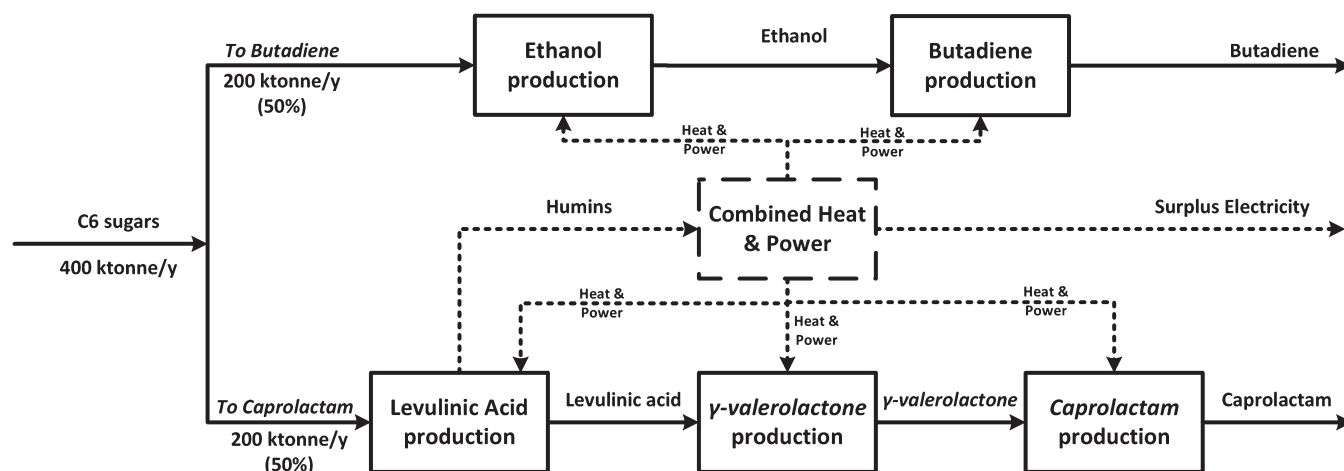


Figure 2. Simplified block diagram of butadiene and caprolactam production from C6 sugars.

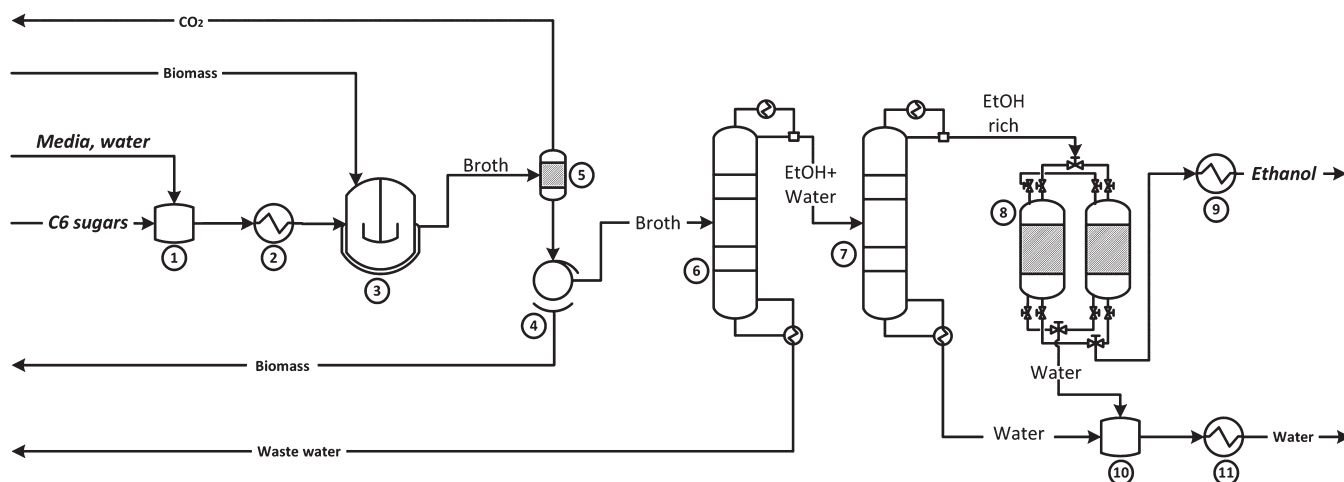


Figure 3. Simplified flowsheet diagram of ethanol production from C6 sugars. Equipment list: 1. Mixer. 2. Heat exchanger. 3. Fermenter. 4. Filter. 5. Knockout drum. 6. Column 1. 7. Column 2. 8. Molecular sieves. 9. Heat exchanger. 10. Mixer. 11. Heat exchanger.

as an additional product. Details of the valorization of humins and process cases are given below.

Butadiene production process

This process comprises two main sections: (i) ethanol production; (ii) butadiene production and recovery. Figure 3 shows the simplified flowsheet of the ethanol production step, consisting of three main steps: fermentation, distillation, and dehydration. The ethanol section was modeled based on the description provided by Quintero *et al.*²⁹ It starts with the reception and conditioning of the C6 sugar stream by diluting it and mixing it with the fermentation media. The fermentation step was modeled assuming 85% of the theoretical yield (ethanol yield: 0.43 kg/kg C6

sugars, theoretical: 0.51 kg/kg C6 sugar) using *S. cerevisiae* as fermenting yeast. Carbon dioxide is produced at a rate of 1.1 kg per kg of ethanol, and yeast at a rate of 0.23 kg per kg of ethanol.³⁰ The fermentation unit works at 31 °C, which is the recommended temperature to avoid yield loss.³⁰ Next, the fermentation broth is sent to a distillation column in which ethanol is concentrated from 8 wt% to 50 wt% in the top stream. The bottom stream contains impurities and it is assumed as wastewater. The concentrated ethanol stream is further concentrated in a second distillation column up to 96 wt% (azeotropic concentration). Finally, ethanol is dehydrated in a sequence of molecular sieves until its concentration reaches 99.7 wt%.

Figure 4 shows a simplified flowsheet of the conversion of ethanol into butadiene. The dehydrated ethanol

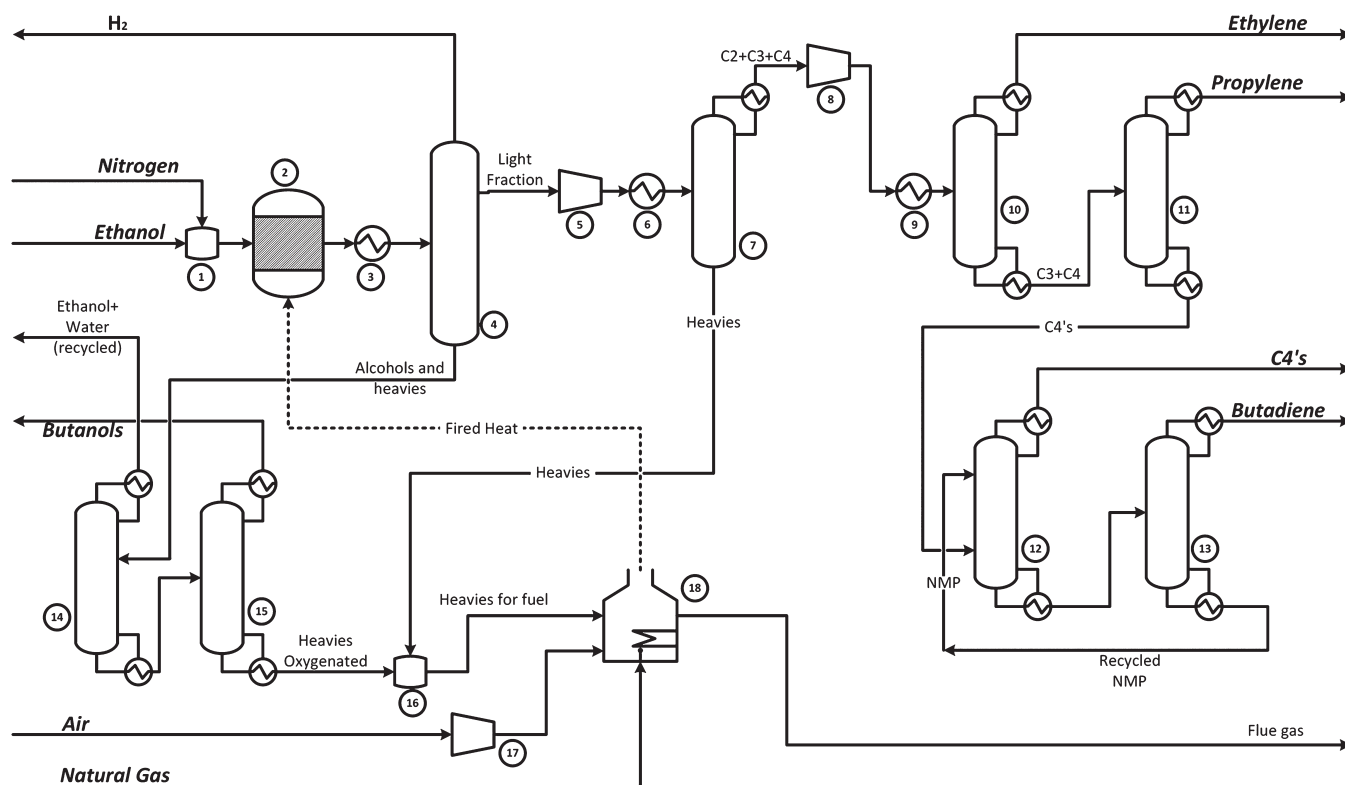


Figure 4. Simplified flowsheet diagram of the conversion of ethanol into butadiene and downstream processing for the recovery of butadiene and co-products. 1. Set up drum. 2. Reactor. 3. Heat exchanger. 4. Flash column. 5. Compressor. 6. Heat exchanger. 7. Distillation column. 8. Compressor. 9. Heat exchanger. 10. Distillation column. 11. Distillation. 12. Extractive distillation column. 13. Distillation column. 14. Distillation column. 15. Distillation column. 16. Mixer drum. 17. Compressor. 18. Furnace.

stream is directed to the butadiene process where ethanol is converted into butadiene and co-products. The base case (Case I) conditions and reactions of the conversion of ethanol into butadiene were gathered by direct communication with experts in butadiene production from Delft University of Technology (Maldonado GC, pers. comm.). The reactor operates at 425 °C and 1 bar. Reactions and ethanol conversion rates used in this study are listed in Table A1 in Appendix A. The reactor effluent contains many compounds, leading to the design of a complex downstream process to recover the butadiene-rich stream. The downstream processing was designed based on an analogy of the traditional petrochemical production of butadiene^{31, 32}. The downstream processing selected, is in principle similar to that proposed by Shylesh *et al.*, (2016)³³ for bio-based butadiene. The first assumption of the downstream processing was that hydrogen produced in the reaction is separated as top product (block 4, Fig. 4). This assumption agrees with the model discussed by Shylesh *et al.*³³ The remaining stream is then separated into light and heavy fractions in a flash column (block 4,

Fig. 4). The heavy fraction contains mainly water, unconverted ethanol, butanols and octanol. This fraction (from block 4 in Fig. 4) is sent to a distillation train (blocks 14 and 15, Fig. 4), where ethanol and water are recovered at the top of the first column and later recycled to the ethanol dehydration step shown in Fig. 3. A fraction of the butanol mixture is recovered at the top of the second column, while the nonrecovered heavies are at the bottom. The butanol-rich stream (a mixture of n-butanol and 2-butanol, at 70/30 mass ratio) is not further split due to the complexity of recovering the individual butanols (i.e., separation of n-butanol from 2-butanol). This stream was instead assumed to be a single product.

The light fraction leaving the flash column (block 4, Fig. 4) is rich in butadiene, ethylene, diethyl ether, propylene, butenes (assumed as a mixture of C4s), and pentene. This stream is compressed up to 10 bar and cooled to 20 °C in order to further separate heavier fractions in a distillation column (block 7, Fig. 4). The bottom stream is rich in diethyl ether and pentane, which are later mixed (block 16, Fig. 4) with the nonrecovered heavies from the butanols

recovery section. The complexity of the heavies stream is considered very high for further downstream processing, and it was therefore assumed that it could be fed to a furnace (block 18, Fig. 3) to provide the required energy to the reactor. The top stream from block 7 (rich in C₂, C₃ and C₄s) is compressed to 25 bar and cooled to 20 °C, before entering a distillation column in which ethylene is recovered as the top product (< 98 wt%) (see block 10, Fig. 4). The bottom product, rich in C₃ and C₄, is sent to a distillation column (block 11, Fig. 4) where propylene is recovered as top product (< 94 wt%). The bottom stream is rich in butenes and butadiene. Due to the similar boiling points, separation using conventional distillation is not possible. In this paper, extractive distillation (blocks 12, 13, Fig. 4) was assumed, using aqueous *n*-methyl-2-pyrrolidone as solvent (NMP).³¹ In the first column, butadiene is recovered as bottom product together with the solvent. The C₄ stream leaves as top product and it was considered as a valuable product (composition 49 wt% 1-butene, 31 wt% 2-butene, 20 wt% isobutene). Finally, the solvent is separated from the butadiene and recycled to the extractive distillation column. The butadiene stream is purified up to concentrations above 99 wt%. The processes shown in Figs 3 and 4 comprise the butadiene production process using C₆ sugars as raw material (called Case I).

Caprolactam production process

The process line for caprolactam production comprises three main sections: (i) levulinic acid production; (ii) γ -valerolactone production, and (iii) caprolactam production and recovery. Figure 5 shows the simplified flowsheet diagram of the production of levulinic acid from C₆ sugars. The production of levulinic acid starts with diluting C₆ sugars in water and adding sulfuric acid (catalyst) prior to the reaction step. Next, the diluted C₆ sugar stream is sent to the reactor, which operates at 200 °C.³⁴ The reaction system consists of the dehydration of C₆ sugars to hydroxymethylfurfural (HMF) (humins formed in this step) and its subsequent conversion into levulinic and formic acid. Product yields were estimated by running the kinetic model reported by Girisuta *et al.*³⁴ Complete conversion of C₆ sugars was assumed in this step with a product distribution of 0.52 kg of levulinic acid, 0.20 kg of formic acid and 0.18 kg of humins per kg fed to the reactor. The resulting mixture was sent to a distillation column where formic acid and water were obtained as top products, and levulinic acid and humins as bottom products. The formic acid stream was further dehydrated using a membrane unit and sold as product. The humins were separated from levulinic acid in a second distillation column.

Figure 6 shows the simplified flowsheet diagram of the production of γ -valerolactone from levulinic acid. The process for producing γ -valerolactone (GVL) from levulinic acid (LA) starts with its dilution in dioxane at a concentration of 10 wt%. The pressure is increased to 10 bar, and the temperature rises to 150 °C, at which point the reaction takes place. The reaction system was modeled on data reported by Ftouni *et al.*²⁴ The reaction is carried out in a Ru/ZrO₂ catalyst, at 150 °C. Reactions are listed in Table A2 in Appendix A. The stream leaving the reactor is cooled and passed through a flash column where the unconverted hydrogen is separated and recycled to the reactor. Next, the GVL diluted in dioxane and water is recovered in a distillation column as a bottom product (with a concentration < 97 wt%). The solvent contains small fractions of water, pentanediol, and methyltetrahydrofuran; thus, a purge is required before recycling the solvent. The purge stream is considered waste.

The caprolactam production process itself comprises three main steps. Step 1 is the production of methyl pentenoates (MPs), which consists of the transesterification of GVL with methanol. This step starts with mixing GVL with methanol, at a methanol/GVL molar ratio of 1.5.¹⁵ The catalyst is *p*-toluenesulfonic acid fed at a ratio of 1 mol per mol of GVL (catalyst is assumed to be recycled to the reactor system). The mixture is heated to 190 °C, and then directed to the transesterification reactor (block 3, Fig. 7). For this step, a conservative approach (assuming a mixture of 3-, and 4-MPs) was followed for the base case (Case III), by considering the formation of 3-MP and 4-MP in a molar ratio of 3 : 1 according to Raoufmoghaddam *et al.*¹⁵ The reactions and conversions are provided in Table A3 in Appendix A. The mixture leaving the reaction system is sent to a distillation train, where both unconverted methanol and GLV are recovered and recycled to the reaction system. The mixture of MPs is sent to the second step, which consists of the aminolysis of MPs into pentenamides (PAs) with ammonia at 80 °C (block 8, Fig. 7). Ammonia is fed at a molar ratio of 5 mol per mol of MPs mixture.¹⁵ Reactions and conversions are also listed in Table A3 in Appendix A. The mixture leaving the reaction system is passed by a flash column (block 9, Fig. 7) where ammonia is recovered and later recycled to the reactor. The liquid stream leaving the flash column is sent to a distillation battery where the methanol produced is recovered and recycled to the transesterification unit, while the PAs are recovered and sent to the last conversion step. The last step is the production of caprolactam (CAL) by the hydroformylation of the PAs into unsaturated caprolactam, and after hydrogenation into CAL. The PAs are first diluted in

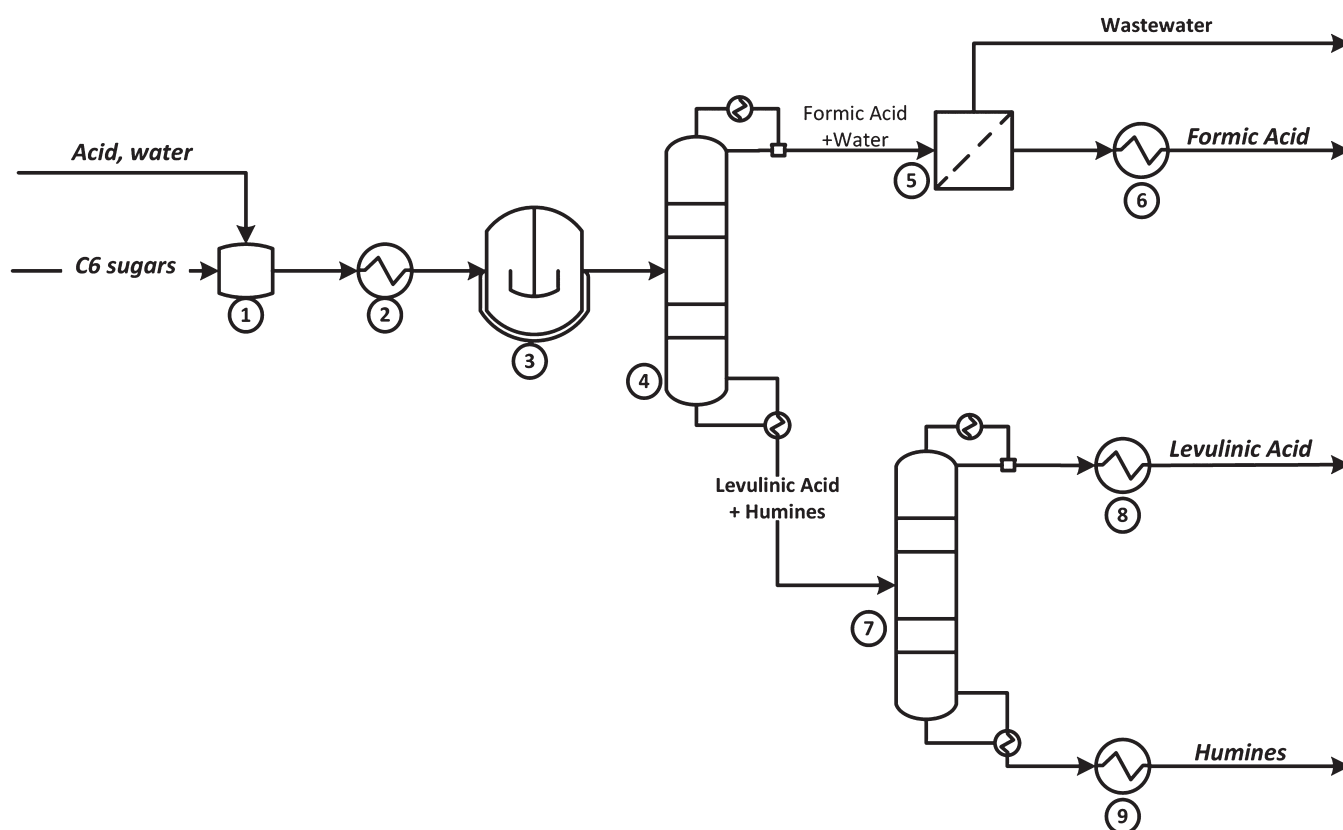


Figure 5. Simplified flowsheet diagram of the production of levulinic acid from C6 sugars. Equipment list: 1. Set up drum. 2. Heat exchanger. 3. Reactor. 4. Distillation column. 5. Membrane unit. 6. Heat exchanger. 7. Distillation column. 8. Heat exchanger. 9. Heat Exchanger

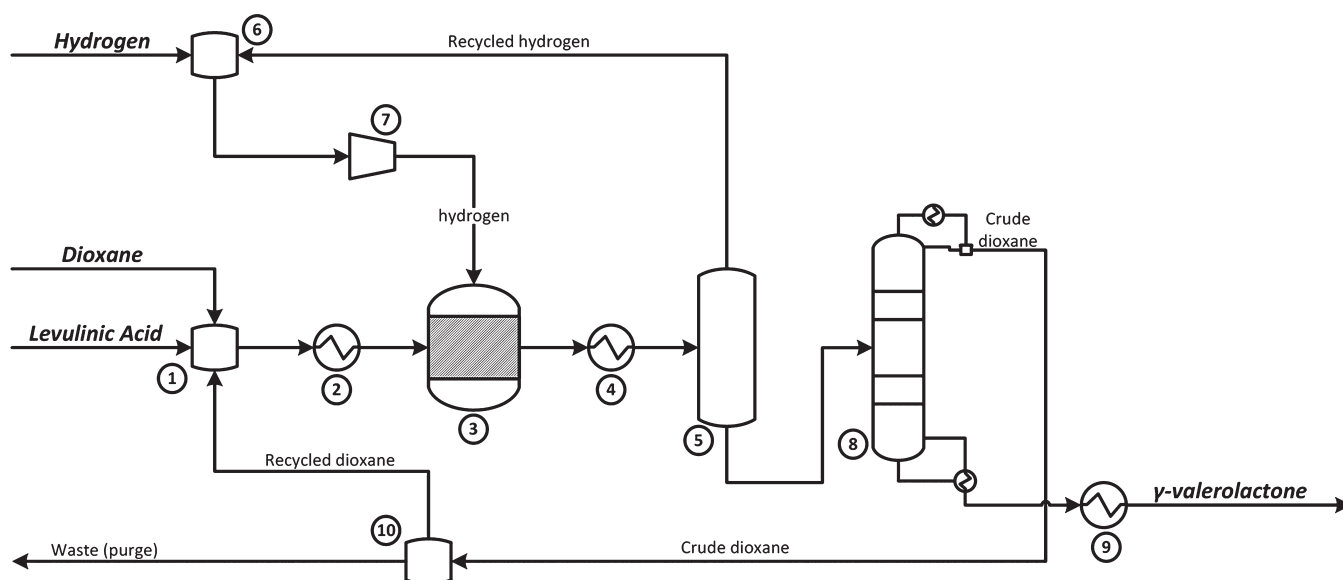


Figure 6. Simplified flowsheet diagram of the production of γ -valerolactone from levulinic acid. Equipment list. 1. Set up drum, 2. Heat Exchanger, 3. Reactor, 4. Heat Exchanger, 5. Flash Column, 6. Mixer drum, 7. Compressor, 8. Distillation Column, 9. Heat Exchanger, 10. Mixer drum.

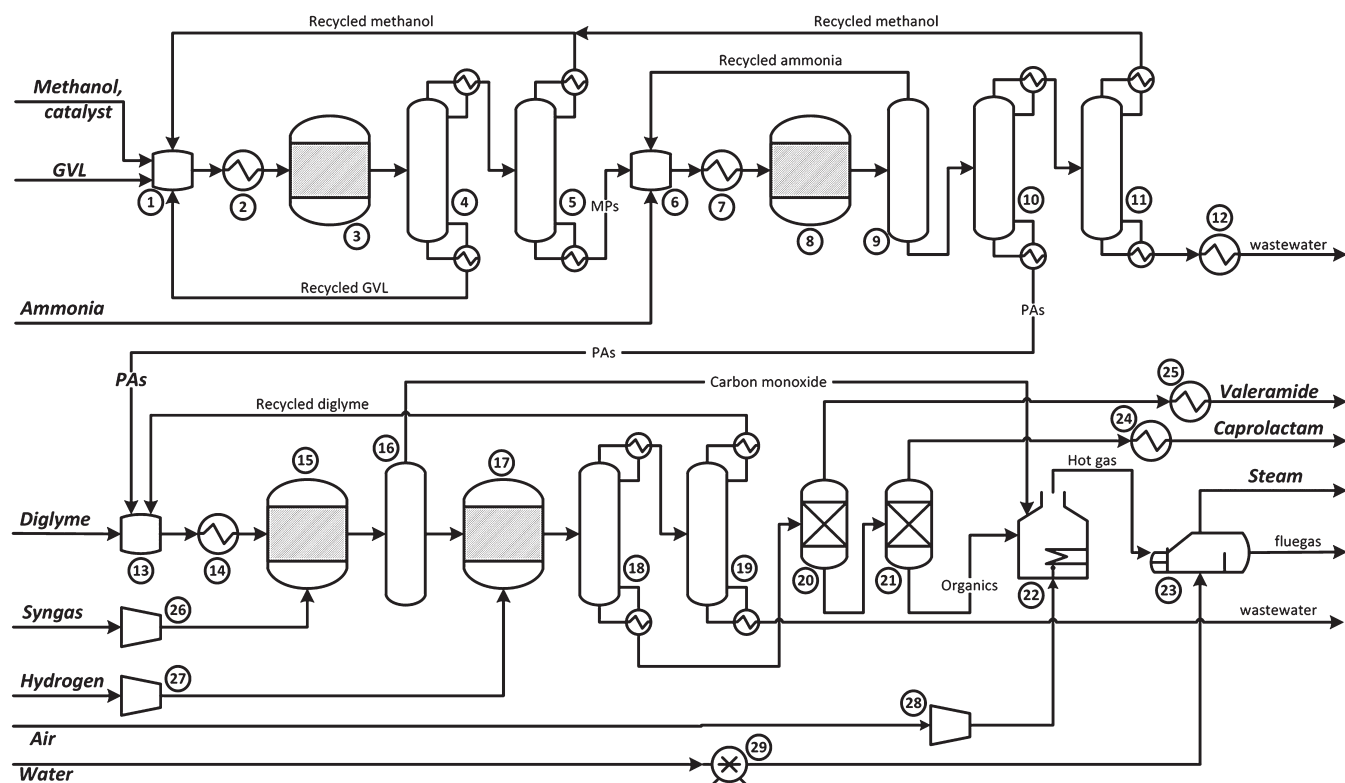


Figure 7. Simplified flow diagram of the production of caprolactam from γ -valerolactone. Equipment list: 1. Set up drum, 2. Heat Exchanger, 3. Reactor, 4. Distillation Column, 5. Distillation Column, 6. Set up drum, 7. Heat Exchanger, 8. Reactor, 9. Flash Column, 10. Distillation Column, 11. Distillation Column, 12. Heat Exchanger, 13. Set up drum, 14. Heat Exchanger, 15. Reactor, 16. Flash Column, 17. Reactor, 18. Distillation Column, 19. Distillation Column, 20. Distillation Column, 21. Adsorption Column, 22. Combustion chamber, 23. Boiler, 24. Heat Exchanger, 25. Heat Exchanger, 26. Compressor, 27. Compressor, 28. Compressor, 29. Pump.

diglyme (concentration of 2 mol/L), heated to 120 °C and converted into unsaturated caprolactam using syngas (CO : H₂ ratio = 1 : 1, 10 bar) (block 15, Fig. 7).¹⁵ The resulting mixture in the hydroformylation step is passed by a flash column to remove excess carbon monoxide (block 16, Fig. 7). Unsaturated caprolactam is hydrogenated (block 17, Fig. 7) at 80 °C using pure hydrogen at 80 bar.¹⁵ The reactions of the caprolactam system were modeled (see Table A3 in Appendix A) according to Raoufmoghaddam *et al.*¹⁵ The stream containing caprolactam is passed by a distillation train (blocks 18 and 19, Fig. 7), where diglyme is recovered and recirculated. The solvent-free caprolactam-rich stream is passed through a series of distillation/adsorption columns (blocks 20 and 21, Fig. 7), where valeramide and caprolactam are recovered as products. From this step, the residue stream is sent to a combustion chamber (mixed with excess carbon monoxide from hydroformylation reaction) to produce steam (blocks 22 and 23, Fig. 7) for consumption in the process. The processes shown in Figs 5, 6

and 7 make up the caprolactam production process using C6 sugars as raw material (Case III).

Process cases and valorization of humins

For the butadiene and caprolactam systems, two cases per process line were considered for the techno-economic assessment. The objective of including two cases per process (i.e., two cases for butadiene and two cases for caprolactam) was to assess the effect of possible changes on the overall performance of both butadiene and caprolactam production. Table 1 summarizes the process cases assessed in this study, where Cases I and II correspond to the butadiene production line, and Cases III and IV correspond to the caprolactam production line.

For the butadiene production line, Case I (the base case) corresponds to the description provided above, whereas Case II uses a different set of data on the conversion of ethanol into butadiene.³³ In this case, the reactor operates

Table 1. Process cases assessed in this study.

Process cases	Butadiene process	Caprolactam process
Case I (base case)	x	
Case II (process with possible improvement)	x	
Case III (base case)		x
Case IV (process with possible improvement)		x

at 250 °C and 1 bar. Reactions and ethanol conversion are listed in Table A1 in the Appendix. Considering that the number of products leaving the reactor differ in comparison to those of Case I, the downstream processing is also modified, where columns 11, 14 and 15 shown in Fig. 3, were left out of the scheme. For Cases I and II, the ethanol production section remains identical.

For the caprolactam production line, Case III (the base case) corresponds to the description provided above. Case IV uses different process sequences in the step from GVL into CAL, where 3-MP is separated from the 4-MP prior to the aminolysis step. The 3-MP is separated from the 4-MP by selective azeotropic distillation (incorporated between blocks 5 and 6 in Fig. 7) and recycled back to the reaction system (transesterification with methanol) to isomerize the 3-MP into 4-MP, and thus increase the yield of 4-PA and subsequently that of caprolactam per GVL fed to the system. This possible improvement is based on the description provided by Raoufmoghaddam *et al.*¹⁵ Reactions are shown in Table A3 in the Appendix.

In addition to the cases described in Table 1, the valorization of humins to produce electricity and heat was considered. Humins are only produced in the caprolactam production process (in the levulinic acid production stage). However, it was assumed that the electricity and heat produced was distributed between the butadiene and caprolactam processes at the same ratio as the input C6 sugar stream was distributed (see above). This means that the production costs of electricity and heat production from humins are distributed between the two process lines (i.e., butadiene and caprolactam). The production of heat and electricity from humins was estimated assuming combined heat and power unit with power and heat efficiencies of 41% and 49%, respectively. Calculations were based on the heating value of humins (23 MJ/kg³⁵). The effect of the valorization of humins is accounted as part of the sensitivity analysis of the cases shown in Table 1. Allocation of heat and power produced from humins is based on the distribution of C6 sugars to each production line.

Economic assessment

The economic assessment involves estimating the capital (CAPEX) and operating (OPEX) expenditures of the processing lines. These expenditures were estimated using information (equipment list, mass, and energy flows) generated in the process modeling stage. In all cases, CAPEX is calculated by adding equipment costs (estimated using the Aspen Economic Analyzer v8.4) and using typical factors for capital investment according to Peters *et al.*³⁶ The factors used in this study can be found in Appendix B. All costs were updated to 2014 prices using the Chemical Engineering Plant Cost Index (CEPCI) and are expressed in euros. When necessary, an average 2014 exchange rate of 0.784 €/USD was applied.

Operational costs (OPEX) include raw materials, utilities, maintenance, labor, fixed costs, general costs, and overheads, and capital depreciation (CAPEX). Raw materials costs were based on mass balances and unit prices (see Table 2). Utilities costs were estimated using energy balances and prices calculated using the equations reported by Ulrich and Vasudevan in 2006³⁷ and updated to 2014 prices (using 2014 CEPCI). Labor costs consisted of operating labor cost (shifts of 8 hours each, 10 operators per shift for both butadiene and caprolactam processes), operating supervision cost, and laboratory charges costs.³⁶ The yearly wage was assumed to be €50 000 per person for all operators of the biorefinery. Additional cost categories such as maintenance, fixed and general, and plant overhead were included in the analysis. These categories were estimated using typical factors as shown in Appendix B.³⁶ These green premiums, CO₂ credits and subsidies were not considered in the analysis. Capital depreciation was estimated using the straight-line method for a depreciation time of 10 years based on suggestions by Peters *et al.*³⁶

To assess the profitability of each system, the net present value (NPV) was used as indicator. The NPV was estimated for a 20-year period using information on capital investment, operating costs and revenues from products by calculating discounted cash flows. The discount rate was set to 10% and income tax to 25% for the Netherlands (NPV calculations after taxes). Each step considered in NPV calculations was based on those reported by Peters *et al.*³⁶ Prices and main economic input parameters used in the assessment are displayed in Table 2.

To have a better understanding of the systems, a sensitivity analysis was carried out to identify which economic parameters affect the NPV the most. Changes to inputs were considered up to $\pm 50\%$ of the reference values shown in Table 2. As part of the sensitivity analysis, the distribution of C6 sugars to caprolactam and butadiene

Table 2. Price inputs used in the economic assessment of the processes butadiene and caprolactam production.

Feature	Value	Unit	Reference
C6 sugars ^a	300	€/tonne	²⁸
Sulfuric acid ^a	220	€/tonne	Average from ³⁸
Ammonia ^a	180	€/tonne	Average from ³⁸
Yeast ^a	1000	€/tonne	³⁹
Dioxane ^a	1670	€/tonne	Average from ³⁸
Methanol ^a	240	€/tonne	⁴⁰
Diglyme ^a	2000	€/tonne	Average from ³⁸
Petrochemical syngas ^a	200	€/tonne	Estimated based on ⁴¹
Butadiene	900	€/tonne	Price index, ⁴²
Ethylene	950	€/tonne	Price index, ⁴²
Propylene	950	€/tonne	Price index, ⁴²
C4s	520	€/tonne	Average price of C4 stream, ⁴²
Hydrogen ^a	1700	€/tonne	⁹
Butanols ^a	500	€/tonne	Average from ³⁸
Cell biomass ^a	10	€/tonne	Assumed as anaerobic digestion digestate based on ⁴³
Formic acid ^a	370	€/tonne	Average from ³⁸
Caprolactam	2000	€/tonne	⁴⁴
Valeramide ^a	300	€/tonne	Conservative estimation based on amide prices ³⁸
Cooling water ^b	0.12	€/m ³	Estimated using equations of ³⁷ and updated to 2014 price
Low-pressure steam ^b	40	€/tonne	Estimated using equations of ³⁷ and updated to 2014 price
Mid-pressure steam ^b	46	€/tonne	Estimated using equations of ³⁷ and updated to 2014 price
Wastewater treatment ^b	0.08	€/m ³	Estimated using equations of ³⁷ and updated to 2014 price
Process water ^b	0.10	€/m ³	Estimated using equations of ³⁷ and updated to 2014 price
Solid disposal ^b	23	€/tonne	Estimated using equations of ³⁷ and updated to 2014 price
Refrigerant ^b	21	€/GJ	Estimated using equations of ³⁷ and updated to 2014 price

^a Prices assumed to be representative for 2014.

^b Prices calculated using the equations proposed by ³⁷, updated to 2014 prices using the CE PCI, and using natural gas as fuel source in the Netherlands (11 €/GJ).⁴⁵

Table 3. Mass balances accounting for key material inputs and outputs of Cases I and II of butadiene production, expressed in ktonne/year.

Cases	Case I		Case II	
Stream	Inputs (ktonne/y)	Outputs (ktonne/y)	Inputs (ktonne/y)	Outputs (ktonne/y)
Raw materials				
C6 sugars ^a	200	—	200	—
Water	998	—	998	—
Ammonia ^b	6	—	6	—
Yeast	2×10^{-1}	—	2×10^{-1}	—
Demineralized water	32	—	25	—
Air	111	—	97	—
Products				
Butadiene ^c	—	24	—	34
Ethylene ^d	—	11	—	9
Propylene ^e	—	1	—	—
C4s ^f	—	3	—	1
Hydrogen	—	1	—	2
Butanols ^g	—	6	—	—
LP steam ^h	—	32	—	25
Cell biomass ⁱ	—	20	—	20
Waste streams				
CO ₂ from fermentation	—	95	—	95
Waste water	—	1033	—	1032
Fluegas ^j	—	121	—	110
Total	1348	1348	1327	1327

^a Stream free of water, C6 sugars purity 100%.

^b Ammonia concentration 25 wt% in water.

^c Butadiene purity 99.7 wt%.

^d Ethylene purity 98.5 wt%.

^e Propylene purity 94.2 wt%.

^f C4's composition: 49 wt% 1-butene, 31 wt% 2-butene, 20 wt% isobutene.

^g Butanols concentration: 70 wt% n-butanol, 30 wt% 2-butanol.

^h LP steam pressure: 3 bar. Product integrated within the process in the energy balance.

ⁱ Cell biomass produced from ethanol fermentation.

^j Flue gas composition: water 11 wt%, CO₂ 16 wt%, O₂ 1 wt%, N₂ 72 wt%.

Results and discussion

Process modeling

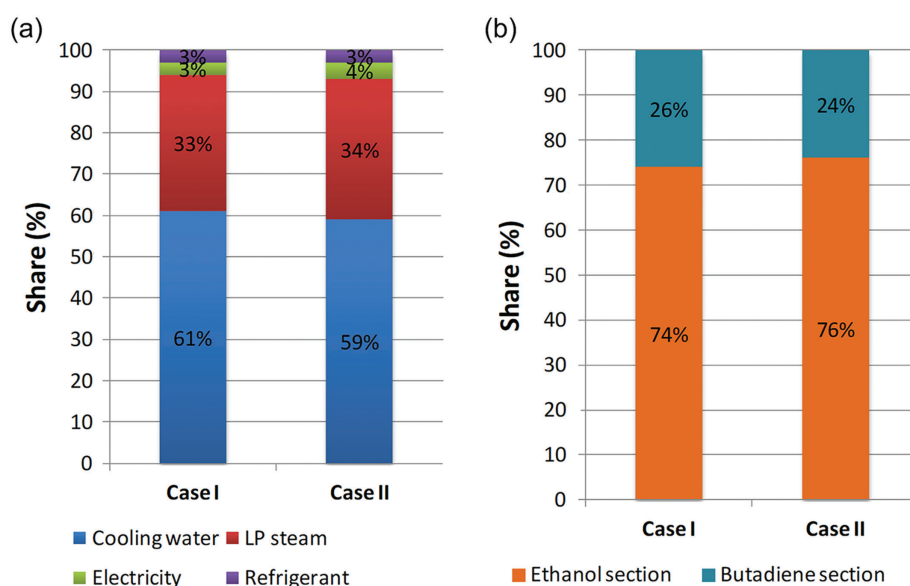
Butadiene process

Table 3 shows the mass balances of the butadiene process for Cases I (base case) and II. All mass balances are expressed on a wet basis, to show all input and output streams for each system. The mass balances provide an

was also assessed, to evaluate the effect of varying the process capacities on the overall economic performance of butadiene and caprolactam production. Escalations of costs were considered linear for OPEX while, for CAPEX components, the six-tenth rule of thumb was applied. The production of electricity and heat from humins was also considered as part of the sensitivity analysis.

Table 4. Energy requirements of Cases I and II of butadiene production, expressed by utility type and process section in TJ/year.

Butadiene production cases		Case I			Case II		
Utility type	Unit	Ethanol section	Butadiene section	Total	Ethanol section	Butadiene section	Total
Cooling water ^a	TJ/y	495	245	740	495	205	700
LP steam ^b	TJ/y	398	—	398	404	—	404
MP steam ^b	TJ/y	—	—	—	—	—	—
Electricity	TJ/y	1×10^{-1}	38	38	1×10^{-1}	48	48
Refrigerant	TJ/y	—	33	33	—	30	30
Total	TJ/y	893	316	1209	899	283	1182

^aCooling water heat capacity: 50 kJ/kg.^bLatent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg.^cNatural gas lower heating value (LHV): 47.1 MJ/kg.**Figure 8. Distribution of total energy requirements for Cases I and II, shown by: (a) utility type; (b) process section.**

indication of the consumption of raw materials and the efficiency of the technology to obtain butadiene and co-products. When comparing the mass balances of the two cases it is noted that the input streams are almost identical with exception of air and demineralized water (lower in Case II), which are used to provide extra energy to the reactor. Comparing the outputs of co-products, it may be seen that the flowrates of products are different with a higher yield of butadiene in Case II in comparison to Case I. For both cases, the product with the highest yield, excluding Low pressure (LP) steam, is butadiene, with 122 and 168 kg per tonne of C6 sugars for Cases I and II, respectively. Only 12% and 17% of the initial mass of C6 sugars is converted into butadiene. The product with the

second highest yield (kg per tonne of C6 sugars) is cell biomass with 99 kg per tonne (for both cases) accounting for approximately 10% of the initial mass of C6 sugars, showing that a large amount of carbon from C6 sugars is lost within ethanol production. In fact, 48% of the initial mass of C6 sugars is converted to CO₂. This aspect can be critical for the subsequent economic and environmental analyses as the overall butadiene processing yield (kg butadiene/tonne C6 sugars) is rather low for such a complex system.

Table 4 shows the energy requirements for the two cases. The total energy requirement of Case I (including ethanol and butadiene sections for all utilities type) corresponds to approximately 50 MJ/kg of butadiene (not allocated). The total energy requirement of Case II (including ethanol and

butadiene sections for all utilities type) corresponds to 35 MJ/kg of butadiene (not allocated), which is 29% lower than the total energy requirements of Case I. This can also be due to a higher butadiene yield in case II compared to case I. Cooling water and refrigerant consumption levels were slightly lower in the butadiene section. A main difference can be seen in LP steam consumption, as that produced in the butadiene process is not sufficient to cover 100% of the demand in the ethanol process. Electricity consumption is 24% higher in Case II than in Case I, mostly due to higher compression requirements for the downstream processing of the gaseous components and air compression as input for the furnace. Note that bio-based butadiene production is still at early development stages and therefore there is high uncertainty on the overall processing efficiencies. Figure 8 shows the contribution of total energy requirements by utility type and process sections for Cases I and II, highlighting the large contribution of cooling water and the large energy requirements to produce ethanol.

When comparing the total energy requirement with the literature (including all utility types), Cespi *et al.*²¹ report a consumption range of 8–10 MJ per kg of butadiene (consumption only for the ethanol to butadiene step of Ostromisslensky and Lebedev processes, respectively), while this study reports of 13 MJ/kg of butadiene for Case I and 8 MJ/kg of butadiene for Case II (consumption only for the butadiene section). Case I shows higher energy requirements (than those reported by Cespi *et al.*²¹) by a factor range of 1.3 to 1.6. Case II shows that the energy requirements are within the range reported by Cespi *et al.*²¹

Caprolactam process

Table 5 shows the mass balances of the caprolactam process for Cases III (base case) and IV (3MPs isomerized to 4MPs before the aminolysis step). In both cases, the annual intake of C6 sugars is identical. By comparing the mass balances of the two cases, the input streams are very similar, with the exception of air, water (related to the production of LP steam) and syngas and hydrogen (slightly higher in Case IV due to higher unsaturated caprolactam production). When comparing the outputs of the co-products, there is no difference in the flowrate of formic acid and water as the process of C6 sugars to levulinic acid step was assumed to be identical in both cases. The flowrates of caprolactam, valeramide, and LP steam vary the most. This is because the conversion into caprolactam is higher for 4PA in comparison to 3PA. There is therefore higher selectivity for caprolactam in Case IV than in Case III. Low pressure steam production is correlated with the nonrecovered organics used to feed the

Table 5. Mass balances accounting for key material inputs and outputs of Cases III and IV of caprolactam production, expressed in ktonne/year.

Cases	Case III		Case IV	
Stream	Inputs (ktonne/y)	Outputs (ktonne/y)	Inputs (ktonne/y)	Outputs (ktonne/y)
Raw materials				
C6 sugars ^a	200	—	200	—
Sulfuric acid	9*10 ⁻²	—	9*10 ⁻²	—
Water	227	—	148	—
Dioxane	1	—	1	—
Hydrogen	3	—	4	—
Methanol	3*10 ⁻³	—	3*10 ⁻³	—
Ammonia ^b	43	—	43	—
Diglyme	4*10 ⁻²	—	4*10 ⁻²	—
Syngas ^c	26	—	27	—
Air	147	—	91	—
Products				
Formic acid	—	41	—	41
Water	—	20	—	20
Caprolactam ^d	—	55	—	88
Valeramide ^e	—	29	—	3
Lp steam ^f	—	181 (192 ^h)	—	102 (192 ^h)
Waste streams				
Humins	—	36	—	36
Waste water	—	117	—	122
Flue gas ^g	—	169	—	101
Total	648	648	513	513

^aThis stream is free of water, C6 sugars purity of 100%.

^bAmmonia concentration is 35 wt% in water.

^cSyngas composition 50 : 50, H₂:CO molar.

^dCaprolactam purity of 99 wt%.

^eValeramide purity of 99wt%.

^fLP steam pressure: 3 bar. Product integrated within the process in the energy balance.

^gFlue gas composition: water 6 wt%, CO₂ 24 wt%, N₂ 67 wt%, NO₂ 3 wt%.

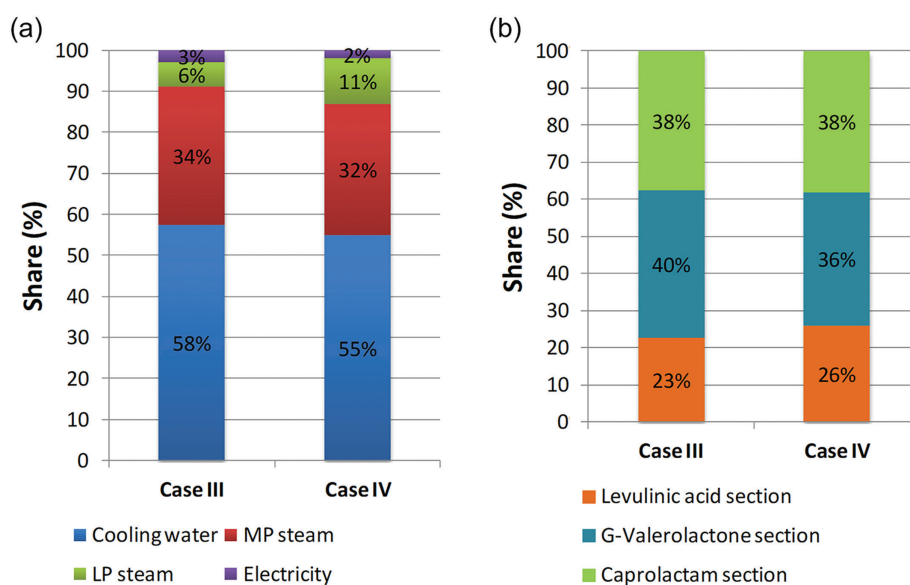
^hAdditional LP steam produced when humins valorization is considered.

combustion chamber (lower in Case IV due to an increase in caprolactam yield). In Case IV, the overall production of caprolactam is 59% higher than in Case III, while the production of valeramide is 91% lower.

In Case III, the product with the highest yield (excluding LP steam and water) is caprolactam with 277 kg per tonne of C6 sugars, followed by formic acid (204 kg per tonne of C6 sugars) and valeramide (145 kg per tonne of C6 sugars). This shows that approximately 28% of the initial mass of C6 sug-

Table 6. Energy requirements of Cases III and IV, expressed by utility type and process section in TJ/year.

Caprolactam production cases		Case III				Case IV			
Utility type	Unit	LA section	GVL section	CAL section	Total	LA section	GVL section	CAL section	Total
Cooling water ^a	TJ/y	468	544	581	1594	468	544	645	1657
LP steam ^b	TJ/y	153	—	—	153 (−408 ^c)	321	—	—	321 (−408 ^c)
MP steam ^b	TJ/y	—	522	415	937	—	522	452	974
Electricity	TJ/y	1	31	44	76 (−341 ^c)	1	31	37	69 (−341 ^c)
Total	TJ/y	622	1098	1040	2760	790	1098	1133	3021

^aCooling water heat capacity: 50 kJ/kg.^bLatent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg.^cTotal electricity and LP steam produced in humins valorization. Negative symbol indicates a production of instead of consumption.**Figure 9. Distribution of total energy requirements for Cases III and IV, shown by: (a) utility type; (b) process section.**

ars is converted into caprolactam. In Case IV, the product with the highest yield is also caprolactam with 441 kg per tonne of C6 sugars (59% higher than Case III), followed by formic acid (204 kg per tonne of C6 sugars) and valeramide (13 kg per tonne of C6 sugars). In Case IV, about 44% of the initial mass of C6 sugars is converted into caprolactam. In terms of waste streams, Case IV shows 19% lower flowrates than those of Case III. The humins produced are equal in the two systems because the levulinic acid process is identical.

Table 6 shows the energy requirements for Cases III and IV. The total energy requirement (including all utilities type) corresponds to 50 MJ/kg of caprolactam for Case III (not allocated). The energy requirements are 9% higher in Case IV than in Case III. Although the annual energy requirements are higher in Case IV than in Case III, the

energy intensity (including all utility types, expressed in MJ per kg of caprolactam) is about one-third lower in Case IV than in Case III (34 MJ/kg) due to a higher CAL yield in Case IV. The cooling water requirement is 4% higher in Case IV than in Case III, while the requirement for LP steam is 109% higher. These higher utility requirements are due to additional separation steps to recover the 3Ms and recycle them to the transesterification step for isomerization into 4MP in Case IV. The electricity consumption in Case IV decreased by 10% in comparison to Case III; however, its contribution is low and thus its effect is marginal. Figure 9 shows the total energy requirements by utility type and process sections for both Cases III and IV, showing a high contribution of the cooling utilities and large contribution for the GVL and CAL sections.

Data on the energy requirements of bio-based caprolactam production are scarce in the literature, so it was not possible to find a comparison with the results of this work. It should be noted that bio-based caprolactam production is at the early stages of development, which brings extra uncertainties to conversion and recovery efficiencies of products and co-products. When considering electricity production from humins, the amount produced is able to cover 100% of electricity requirements in Cases I and II of butadiene production and III and IV of caprolactam production. The surplus electricity is considered as a by-product (227 TJ/y).

Economic analysis

The butadiene process

Table 7 shows the CAPEX, OPEX, revenues and NPV for each case. In Cases I and II, the fixed capital investment of the ethanol section remained equal (55 M€). The fixed capital investment of the butadiene section is 75 M€ for Case I and 80 M€ in Case II (6% higher). This difference is basically due to a higher butadiene production rate in

Table 7. Annualized operational costs, revenues, fixed capital investment and net present value of Cases I and II of butadiene production.

Feature	Case I		Case II	
	M€/year	Share (%)	M€/year	Share (%)
Operating costs (OPEX)				
Raw materials	61.4	63	61.4	62
Utilities	11.2	11	11.4	12
Maintenance	9.0	9	9.3	9
Labor	1.95	2	1.95	2
Fixed and general	8.4	9	8.7	9
Overhead	5.7	6	5.9	6
Total	97.7	100	98.7	100
Revenues				
Butadiene	22.0	55	30.2	71
Ethylene	10.5	26	8.5	20
Propylene	1.1	3	0.0	0
C4s	1.5	4	0.5	1
Hydrogen	1.5	4	3.1	7
Butanols	3.1	8	0.0	0
Cell biomass	0.2	0	0.2	0
Total	40.0	100	42.6	100
Fixed capital investment (CAPEX)				
M€	130		135	
Net present value after taxes ^a				
M€	−647		−642	
^a NPV at the end of project's lifetime.				

^a NPV at the end of project's lifetime.

Case II, despite the reduction in process units (columns 11, 14 and 15 shown in Fig. 4 were left out of the scheme). Note that the bio-based butadiene process is still at early development stages, thus bringing large uncertainties in capital costs. Literature reporting capital costs of ethanol associated with the butadiene process is limited, confirming the importance of including this as part of the sensitivity analysis. In the two cases, the aspects that contribute the most to OPEX are raw materials, and utilities. OPEX are rather similar for Cases I and II. In terms of revenues, Case II shows slightly higher values, with butadiene as the major contributor, and in both cases ethylene as the second major contributor. This shows the high correlation between the revenues of butadiene and the feasibility of the system. Note that an important amount of cell biomass is produced in the ethanol process and, as previously mentioned, it is the product with the second highest yield (after butadiene). However, from an economic perspective, its contribution to revenues is marginal due to its low price. Another option to improve the overall economics of the butadiene process is to capture the CO₂ produced in the ethanol process (i.e., during fermentation) and generate additional income (e.g., bio-CCS, CO₂ utilization); however, this is outside the scope of the current assessment. (This might also represent additional CAPEX.)

The NPV results (see Table 7) show negative values for Cases I and II, implying that, with the data considered in this study, both processes are economically unfeasible. OPEX are much higher than revenues in Cases I and II, and added to capital investment, their economic unfeasibility can be seen. Note that both butadiene processes show similar NPV values, thus suggesting robustness with regard to the unfeasibility of butadiene production from C6 sugars at current butadiene prices. To break even (assuming all other parameters fixed, such as co-products prices), the selling price of butadiene needs to be 4369 €/tonne for Case I and 3406 €/tonne for Case II. This represents an increase of a factor of 3.8–4.9 in comparison to the reference price (900 €/tonne, see Table 7). The literature also discusses instances where the production cost price of butadiene is higher than its reference (market) price. For instance, Farzad *et al.*²² reported higher production cost prices than market butadiene prices by a factor of 3.0–3.3.

Sensitivity analysis

The sensitivity analyses focus on the NPV. The results for Case I (see Fig. 10a) suggest that the parameters that influence the NPV most are the C6 sugars price, capital investment and the butadiene price. The effect of the C6 sugars price and capital investment is similar, where increases

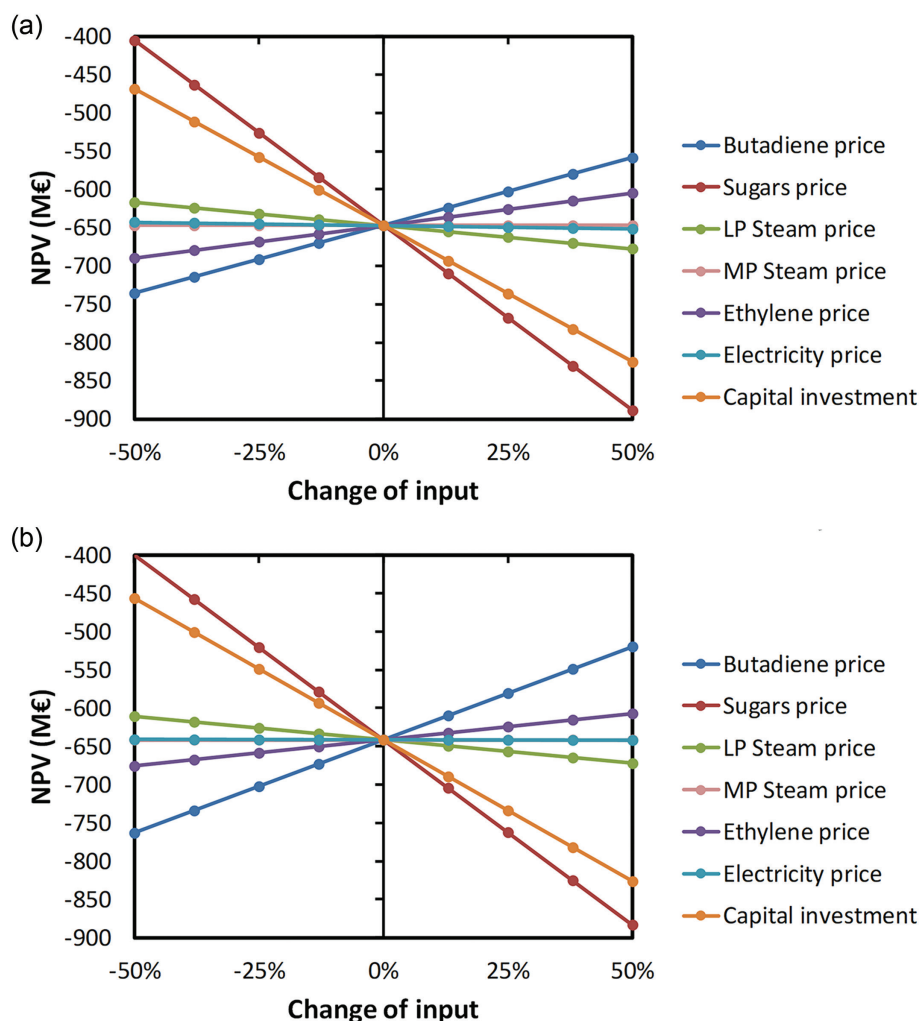


Figure 10. Results of sensitivity analysis on economic parameters of butadiene production: (a) Case I, (b) Case II.

over the reference values will lead to even more unfeasible scenarios, and decreases may bring the system closer to the break-even point. However, even with drastic decreases of 100% in these two parameters (independently of each other), the system is not able to break even. The effect of both butadiene and ethylene prices is not particularly high in comparison with C6 sugars and capital investment of the butadiene section. As mentioned previously, the price of butadiene needs to be up to 380–490% higher than the reference value to break even. This is very unlikely because a price increase would only be possible by including high extra premiums, and even fluctuations on butadiene prices are unlikely to reach such a high value.

For Case II, the results of the sensitivity analysis (see Figure 10(b)) are very similar to those of Case I. The parameters that affect the NPV the most are the price of C6 sugars, capital investment, and the butadiene price.

The effect of changes in the price of C6 sugars and capital investment follow the same trend as those of Case I. The effect of changes in butadiene price is stronger in Case II, mostly because the system produces a higher butadiene flowrate than in Case I. The behavior of the remaining parameters is similar. Overall, Cases I and II are very sensitive to changes in most economic parameters, thus suggesting higher risks to the implementation of this technology. The butadiene production process does not appear robust in economic terms.

Figure 11 shows the effect of varying the distribution of C6 sugars in the butadiene and caprolactam processes. The production cost price (Fig. 11(b)) of butadiene may be lower when the intake capacity of C6 sugars increases. For instance, when 100% of C6 sugars to butadiene and caprolactam are sent to the butadiene process (400 ktonne/year C6 sugar), the production cost price of butadiene decreases

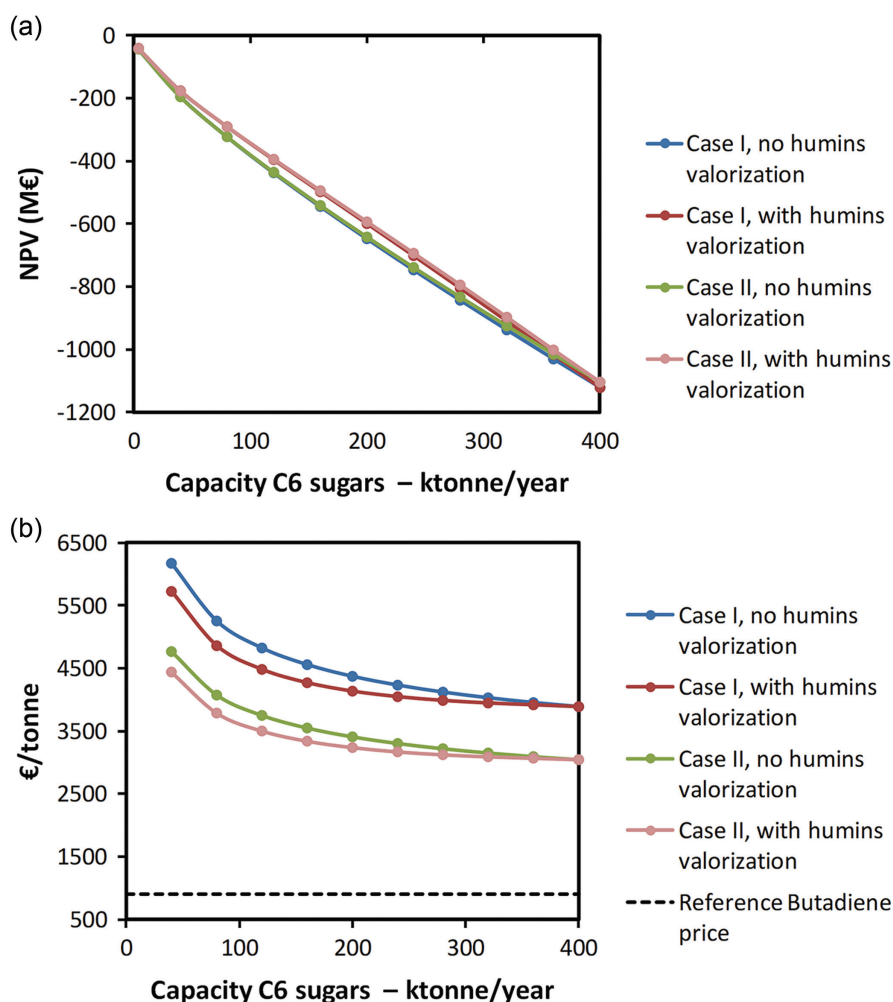


Figure 11. Results of sensitivity analysis on varying the amount of C6 sugars sent to the butadiene process. (a) effect on NPV; (b) effect on production cost price (reference price 900 €/tonne).

in comparison to the base case (3887 €/tonne for Case I and 3042 €/tonne for Case II). This suggests benefits from economies of scale. However, cost prices are still a factor, 3.4–4.3 higher than the reference price of butadiene. Even increasing the plant capacity to take advantage of economies of scale is therefore not sufficient to compensate for the high costs related to the butadiene process cases. This implies that the NPV becomes even more negative when the process capacity increases (Fig. 11(a)). In terms of butadiene's production costs price (at NPV = 0, see Figure 11(b)), it tends to decrease when higher capacities are used. Nevertheless, cost prices are always above the butadiene reference market price for all cases. The valorization of humins does not have a strong effect on the systems, and the difference in NPV, when electricity from humins is included, is barely noticeable.

The caprolactam process

Table 8 shows the CAPEX, OPEX, revenues, and NPV for Cases III and IV of caprolactam production. In the two cases, the fixed capital investment of the levulinic acid and GVL sections are identical (19 and 38 M€, respectively). The fixed capital investment of the caprolactam section varies from Case III to Case IV, with Case IV being higher by 32% (Case III: 81M€, Case IV: 107 M€). This increase is due to the inclusion of additional process steps to isolate the 3MP from the MP mixture and recycle the 3MP for isomerization into 4MP prior to the aminolysis step.

In both cases, the aspects that contribute the most to OPEX are raw materials and utilities (although this is not surprising for a chemical process). When comparing OPEX, those of case IV are slightly higher than those of Case III due

Table 8. Annualized production costs, revenues and Net Present Value of Cases III and IV of caprolactam production.

Feature	Case III		Case IV	
	M€/year	Share (%)	M€/year	Share (%)
Operating costs (OPEX)				
Raw materials	80.0	58	80.4	55
Utilities	32.5	23	36.5	25
Maintenance	9.5	7	11.3	8
Labor	1.95	1	1.95	1
Fixed and general	8.9	6	10.5	7
Overhead	6.0	4	6.9	5
Total	138.8	100	147.5	100
Revenues				
Formic acid	15.1	11	15.1	8
Caprolactam	110.6	82	176.4	92
Valeramide	8.7	6	0.8	0
Total	134.4	100	192.3	100
Fixed capital investment (CAPEX)				
M€	138		164	
Net present value after taxes ^a				
M€	-229		67	

^a NPV at the end of project's lifetime.

to the higher cost of utilities related to the additional process steps to recover the 3MP fraction of the transesterification step. In terms of revenues, the product that contributes the most is caprolactam with 82% and 92% in Cases III and IV, respectively. When comparing cases, Case IV has 43% higher revenues than Case III because more caprolactam is produced as a consequence of the isomerization of 3MP into 4MP prior to the aminolysis step. Note that in Case III (see Table 8), revenues are lower than OPEX, although, in Case IV, revenues are higher than OPEX. The latter suggests that Case IV has a better outlook for economic feasibility. Nevertheless, it should be borne in mind that the effect of CAPEX on the NPV can be stronger than OPEX.

The NPV results (see Table 8) show a negative value for Case III (unfeasible) and positive for Case IV (feasible). For Case III to break even (assuming all other parameters fixed, such as co-products prices), the production cost price of caprolactam needs to be 2595 €/tonne, which is 30% higher than the reference price (2000 €/tonne). The production cost price remains higher than the reference caprolactam price; however, it is in a more reasonable range than the higher cost price of butadiene compared to its reference price. Reductions in OPEX may make the system economically feasible (Case III). In Case IV, the pro-

duction cost price of caprolactam is 1875 €/tonne, which is 6% lower than the reference caprolactam price. The NPV results suggest that including 3MP for isomerization into 4MP before the aminolysis step represents an important improvement for caprolactam production.

Sensitivity analysis

The results for Case III (see Figure 12(a)) suggest that the parameters that influence NPV the most are caprolactam, C6 sugar prices, and CAPEX. The effect of changes in caprolactam price is clearly stronger than that for other parameters. An increase of caprolactam price above 30% will make the system economically feasible. Similarly, to break even, the price of C6 sugars needs to be 57% lower than the reference value shown in Table 2, while increasing the price leads to a less feasible case. The effects of the remaining parameters are similar and do not strongly affect the system's economic feasibility. The results of the sensitivity analysis of Case IV show a rather similar trend to those of Case III but with a positive NPV at 0% change. The results for Case IV (see Figure 12(b)) indicate that the parameter that influences NPV the most is the caprolactam price. The effect of the caprolactam price is clearly stronger in Case IV than in Case III. A decrease of the caprolactam price over 5%, results in an unfeasible scenario. However, increases above the reference price will improve the overall economic performance of the system. The effect of the C6 sugar price and CAPEX is almost identical. Increases over 25% in either of these two parameters (independent of each other and leaving the others fixed) lead to unfeasible scenarios. However, a reduction in C6 sugar prices would further benefit the system's economic performance. The effect of the remaining parameters is rather similar and does not have a strong influence on the system. In summary, Cases III and IV for show that caprolactam production is robust and basically depends on the state of the caprolactam market instead of multiple undeveloped markets of other co-products. However, this also poses some risk in the event that prices of caprolactam do not remain equal to or above the reference price considered in this study. Improvements in NPV would ultimately represent a reduction in the cost price of caprolactam.

Figure 13a shows the effect on the NPV of varying the capacity of C6 sugars intake to the caprolactam process. This analysis also includes the effect of the valorization of humins for heat and power production. The results suggest that Case IV benefits from the economies of scale, operating at larger capacities than those of the base case (200 ktonne/y of C6 sugars). At an input of C6 sugars capacity lower than 148 ktonne/y the system starts to be unfeasible.

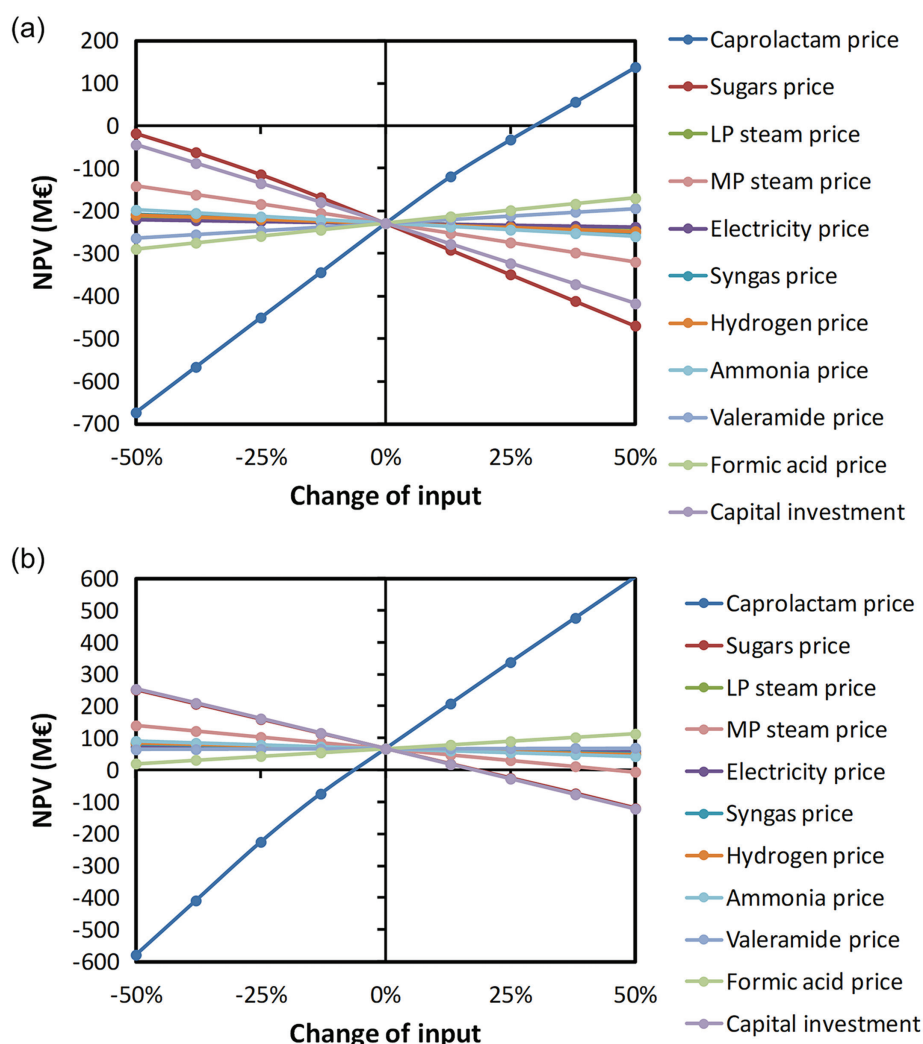


Figure 12. Results of sensitivity analysis on economic parameters of caprolactam production: (a) Case III; (b) Case IV.

For Case III, the system remains unfeasible; however, the trend of the curves suggests that if C6 sugar intake capacity could be increased, the system may break even if valorization of humins is included. The effect of heat and power production from humins starts to be noticeable when the capacity of C6 sugars intake is above 120 ktonne/y (which applies for Cases III and IV). This has to do with the availability of humins and the synergy between the butadiene and caprolactam processes (see Fig. 2) because, as assumed in this study, the intake C6 sugar capacity of the butadiene process decreases when the intake of the caprolactam process increases (distribution of C6 sugars). If caprolactam is produced in larger quantities, therefore, more humins are available for heat and power production. The effect of humins valorization has a positive effect on the overall economic performance of both Cases III and IV. The

main reason is due to the savings in purchased steam and electricity (as discussed above, see Table 6), which reduces utility costs (saving up to 2.3 M€/y for Cases I to IV, with base case C6 sugars distribution). The revenues from surplus electricity also represent an extra 5 M€/y (at base case conditions) to Cases I and II, and 5 M€/y to the revenues of Cases III and IV. Nevertheless, it should be borne in mind that 16 M€ of additional CAPEX are required to produce heat and power from humins. The increase in CAPEX is allocated to both butadiene and caprolactam processes depending on the distribution of C6 sugars to each process, which in base-case conditions is 50% (i.e., extra CAPEX of 8 M€ to the butadiene process and 8 M€ to the caprolactam process). Although the production trains were analyzed separately, the strategy of a multiproduct biorefinery system was considered as central to this study.

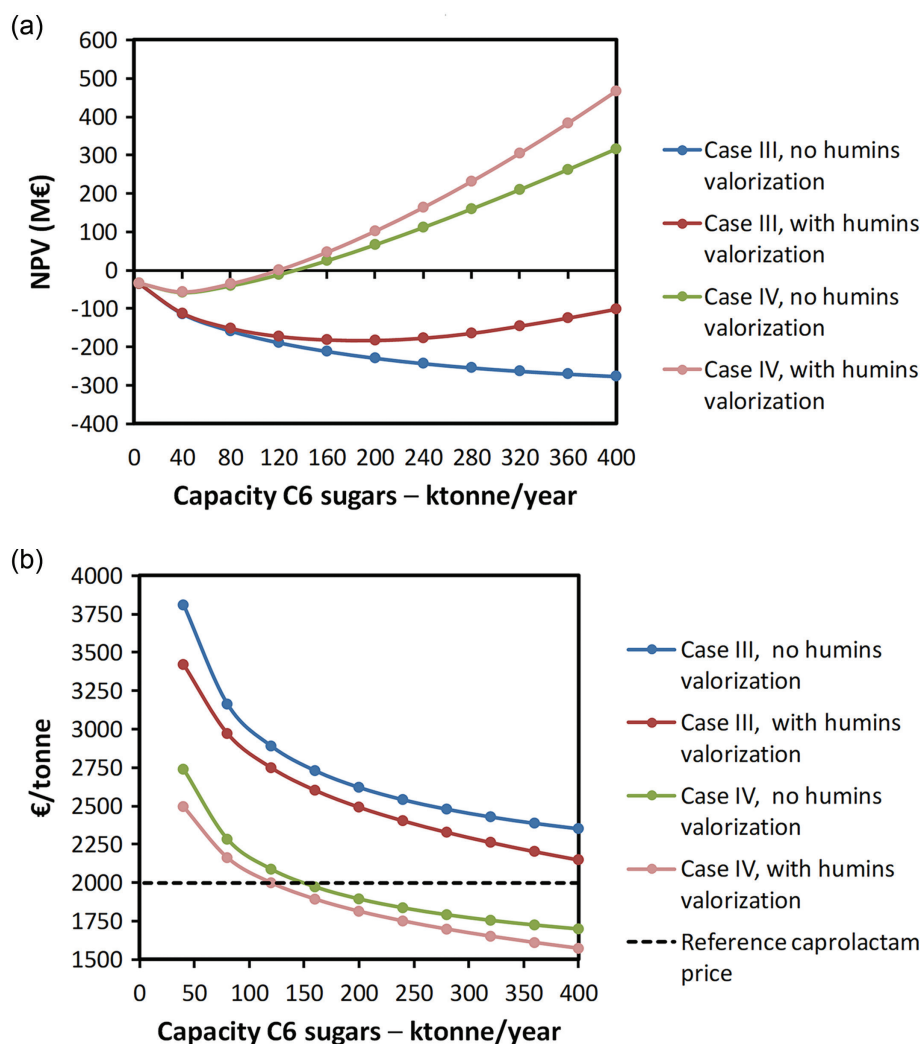


Figure 13. Results of sensitivity analysis on varying the amount of C6 sugars sent to the caprolactam process: (a) effect on NPV; (b) effect on minimum selling price (reference price 2000 €/tonne).

Figure 13(b) shows how the production cost price (at NPV = 0) of caprolactam decreases as the input capacity of C6 sugars increases. For Case IV (with and without valorization of humins), the production cost price starts to be higher than the reference price at capacities lower than 130 ktonne/y. In Case III, the production cost price is always higher than the reference price but getting closer as the production capacity increases. Both Cases III and IV are benefit strongly from economies of scale and from the valorization of humins to produce heat and electricity.

Conclusions

The aims of this study were to investigate the techno-economic performance of the production lines for butadi-

ene and caprolactam from C6 sugars, and to assess which of the two was economically attractive. In terms of energy intensity, both production lines perform similarly ranging from 34–50 MJ/kg of main product (depending on conditions). In terms of process yields (expressed as kg of product per kg of C6 sugars), that of caprolactam is a factor 1.6–3.6 higher than that of butadiene. In the butadiene process, a large amount of the carbon mass of C6 sugars goes into the cell biomass and carbon dioxide (both produced during the ethanol production process), which are streams with low value added.

From an economic point of view, the butadiene process shows a negative performance even when the system is improved (Case II) to enhance the selectivity to butadiene and to reduce the number of co-products (implying a

reduction in energy intensity and capital investment, compared to Case I). The economic performance of the butadiene process is highly dependent on the revenues of butadiene and ethylene, and highly sensitive to changes in C6 sugar prices and capital investment. However, even with drastic changes in these parameters, the butadiene production line remains unfeasible. Butadiene production cost is 3–5 times higher (depending on conditions) than its reference market price (900 €/tonne). This highlights the efforts needed to improve the overall efficiency of the butadiene process and to find alternatives to promote the bio-based butadiene market, such as policy incentives (e.g., green premiums). The use of cheaper raw materials also plays a crucial role in the economic performance of chemicals such as butadiene, for instance by directly starting from lignocellulosic biomass instead of C6 sugars. This would help to reduce extra logistics costs of dealing with intermediate platform chemicals, and would take advantage of revenues from co-products at the pre-treatment stage. This integration approach could also be beneficial in the case of additional heat and mass integration strategies, which can play a major role in decreasing OPEX. Nevertheless, it should be borne in mind that this integration strategy may only be practicable in specific countries/regions where the availability of biomass is not a major issue.

Under base case conditions (Case III), caprolactam production also seems unfeasible; however, changes in prices such as a reduction in the price of feedstock and an increase in caprolactam prices may make the system become feasible. The caprolactam production cost for Case III is 30% higher than its reference selling price (2000 €/tonne). Moreover, in the case in which the processing line of caprolactam improves its yield (Case IV, yield improved by 60% compared to Case III), the system becomes economically feasible with production costs 6% lower than its reference market price (2000 €/tonne). Additional integration strategies can also work in the case of caprolactam.

Including heat and power production from humins seems to have a positive effect on the overall economic performance of the caprolactam production process (independently of the case), and production costs are further decreased by savings on external utilities (i.e., heat and power), purchases and revenues from surplus electricity. Production costs of both butadiene and caprolactam were reduced when the processing capacity for C6 sugars was increased, reflecting benefits from economies of scale. However, only the production costs of caprolactam are lower than the reference price. From an integrated biorefinery perspective, a biorefinery co-producing butadiene from C6 sugars is not economically interesting; however,

it is open to improvements and analysis in other contexts. Overall, the caprolactam production line shows higher economic potential in comparison with that of butadiene.

Acknowledgements

This research was performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science. Project number 053.70.381.

References

1. Cherubini F, The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers Manage* **51**(7):1412–1421 (2010).
2. Hossain GS, Liu L and Du GC, Industrial bioprocesses and the biorefinery concept, in *Current Developments in Biotechnology and Bioengineering*, ed. by Larroche C, Sanromán MA, Du G, Pandey A. Elsevier, Amsterdam, pp. 3–27 (2017).
3. Moncada J, Tamayo JA and Cardona CA, Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery. *Chem Eng Sci* **118**:126–140 (2014).
4. Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R *et al.* Toward a common classification approach for biorefinery systems. *Biofuels Bioprod Biorefin* **3**(5):534–546 (2009).
5. de Jong E, Higson A, Walsh P and Wellisch M, Bio-based Chemicals Value Added Products from Biorefineries. Report of the IEA Bioenergy, Task42 Biorefinery (2012). Available at: <http://www.ieabioenergy.com/publications/bio-based-chemicals-value-added-products-from-biorefineries/>
6. Dusselier M, Mascal M and Sels BF, Top chemical opportunities from carbohydrate biomass: A chemist's view of the biorefinery, in *Selective Catalysis for Renewable Feedstocks and Chemicals*, ed. by Nicholas KM. Springer International Publishing, Cham, pp. 1–40 (2014).
7. Bozell JJ and Petersen GR, Technology development for the production of biobased products from biorefinery carbohydrates – the US Department of Energy's 'Top 10' revisited. *Green Chem* **12**(4):539–554 (2010).
8. Moncada J, Posada JA and Ramírez A, Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. *Biofuels Bioprod Biorefin* **9**:722–748 (2015).
9. Posada JA, Patel AD, Roes A, Blok K, Faaij AP and Patel MK, Potential of bioethanol as a chemical building block for biorefineries: preliminary sustainability assessment of 12 bioethanol-based products. *Bioresour Technol* **135**:490–499 (2013).
10. Hayes DJ, Fitzpatrick S, Hayes MHB and Ross JRH, The biofine process – production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks. *Biorefineries-Industrial Processes and Products*, ed. by Kamm B, Gruber PR, and Kamm M. Wiley-VCH Verlag GmbH, Weinheim, pp. 139–164 (2008).
11. Hayes DJ, Fitzpatrick S, Hayes MH and Ross JR, The Biofine process – Production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks. *Biorefineries – Industrial Processes and Product* **1**:139–164 (2006).

12. Angelici C, Weckhuysen BM and Bruijninx PC, Chemocatalytic conversion of ethanol into butadiene and other bulk chemicals. *ChemSusChem* **6**(9):1595–1614 (2013).
13. Makshina EV, Janssens W, Sels BF and Jacobs PA, Catalytic study of the conversion of ethanol into 1,3-butadiene. *Catal Today* **198**(1):338–344 (2012).
14. Kim T-W, Kim J-W, Kim S-Y, Chae H-J, Kim J-R, Jeong S-Y *et al.*, Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported spherical silica catalysts for circulating fluidized bed. *Chem Eng J* **278**:217–223 (2015).
15. Raoufmoghaddam S, Rood M, Buijze FK, Drent E and Bouwman E, Catalytic conversion of γ -valerolactone to ϵ -caprolactam: towards nylon from renewable feedstock. *ChemSusChem* **7**(7):1984–1990 (2014).
16. Hong J and Xu X, Environmental impact assessment of caprolactam production – a case study in China. *J Cleaner Prod* **27**:103–108 (2012).
17. Wang Y and Liu S, Butadiene production from ethanol. *J Bioproc Eng Bioref* **1**(1):33–43 (2012).
18. Kyriienko PI, Larina OV, Soloviev SO, Orlyk SM and Dzwigaj S, High selectivity of TaSiBEA zeolite catalysts in 1,3-butadiene production from ethanol and acetaldehyde mixture. *Catal Commun* **77**:123–126 (2016).
19. Chae H-J, Kim T-W, Moon Y-K, Kim H-K, Jeong K-E, Kim C-U *et al.*, Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts. *Appl Catal B* **150**:596–604 (2014).
20. Patel AD, Meesters K, den Uil H, de Jong E, Blok K and Patel MK, Sustainability assessment of novel chemical processes at early stage: application to biobased processes. *Energy Environ Sci* **5**(9):8430–8444 (2012).
21. Cespi D, Passarini F, Vassura I and Cavani F, Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. *Green Chem* **18**(6):1625–1638 (2016).
22. Farzad S, Mandegari MA and Görgens JF, Integrated techno-economic and environmental analysis of butadiene production from biomass. *Bioresour Technol* **239**:37–48 (2017).
23. Girisuta B and Heeres HJ, Levulinic acid from biomass: synthesis and applications, in *Production of Platform Chemicals from Sustainable Resources*, ed. by Fang Z, Smith JRL and Qi X. Springer Singapore, Singapore, pp. 143–169 (2017).
24. Ftouni J, Muñoz-Murillo A, Goryachev A, Hofmann JP, Hensen EJM, Lu L *et al.*, ZrO_2 is preferred over TiO_2 as support for the Ru-catalyzed hydrogenation of levulinic acid to γ -valerolactone. *ACS Catal* **6**(8):5462–5472 (2016).
25. Abdelrahman OA, Heyden A and Bond JQ, Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ -valerolactone over Ru/C. *ACS Catal* **4**(4):1171–1181 (2014).
26. Han J, Biorenewable Strategy for Catalytic ϵ -Caprolactam Production Using Cellulose- and Hemicellulose-Derived γ -Valerolactone. *ACS Sustainable Chem Eng* **5**(2):1892–1898 (2017).
27. Wooley RJ and Putsche V, Development of an ASPEN PLUS Physical Property Database for Biofuels Components. [Online]. National Renewable Energy Laboratory (1996). Available at: <http://infohouse.p2ric.org/ref/22/21210.pdf> [March 1, 2018].
28. Moncada J, Vural Gursel I, Huijgen WJ, Dijkstra JW and Ramírez A, Techno-economic and ex-ante environmental assessment of C6 sugars production from spruce and corn. Comparison of organosolv and wet milling technologies. *J Cleaner Prod* **170**:610–624 (2018).
29. Quintero J, Montoya M, Sánchez OJ, Giraldo O and Cardona C, Fuel ethanol production from sugarcane and corn: Comparative analysis for a Colombian case. *Energy* **33**(3):385–399 (2008).
30. Rivera EC, Costa AC, Atala DI, Maugeri F, Maciel MRW and Maciel Filho R, Evaluation of optimization techniques for parameter estimation: Application to ethanol fermentation considering the effect of temperature. *Process Biochem* **41**(7):1682–1687 (2006).
31. White WC, Butadiene production process overview. *Chem Biol Interact* **166**(1–3):10–14 (2007).
32. Eldridge RB, Olefin/paraffin separation technology: a review. *Ind Eng Chem Chem Res* **32**(10):2208–2212 (1993).
33. Shylesh S, Gokhale AA, Scown CD, Kim D, Ho CR and Bell AT, From sugars to wheels: The conversion of ethanol to 1, 3-butadiene over metal-promoted magnesia-silicate catalysts. *ChemSusChem* **9**(12):1462–1472 (2016).
34. Girisuta B, Janssen L and Heeres HJ, Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. *Chem Eng Res Des* **84**(5):339–349 (2006).
35. Mija A, Van Der Waal J, Pin J-M, Guigo N and De Jong E (eds.), Humins as promising material for producing sustainable polysaccharide-derived building materials. First International Conference on Bio-based Building Materials Clermont-Ferrand, France, (2015).
36. Peters M, Timmerhaus K and West R, *Plant Design and Economics for Chemical Engineers*. McGraw Hill, New York, NY (2003).
37. Ulrich GD and Vasudevan PT, How to estimate utility costs. *Chem Eng* **113**(4):66 (2006).
38. Alibaba, Average Prices of Chemicals. [Online]. (2015). Available at: https://www.alibaba.com/Chemicals_p8. [Accessed: 15 July 2015]
39. Nitzsche R, Budzinski M and Gröngroft A, Techno-economic assessment of a wood-based biorefinery concept for the production of polymer-grade ethylene, organosolv lignin and fuel. *Bioresour Technol* **200**:928–939 (2016).
40. Methanex, *Methanol Price*. [Online]. (2016). Available at: <https://www.methanex.com/our-business/pricing>. [Accessed: June 6 2016]
41. Pei P, Korom SF, Ling K and Nasah J, Cost comparison of syngas production from natural gas conversion and underground coal gasification. *Mitig Adapt Strategies Glob Chang* **21**(4):629–643 (2016).
42. Platts, *Platts Price Index*. [Online]. (2014). Available at: <https://www.platts.com/commodity/petrochemicals>. [Accessed: September 23 2016]
43. Gebrezgabher SA, Meuwissen MPM, Prins BAM, Lansink AGJMO, Economic analysis of anaerobic digestion – a case of green power biogas plant in the Netherlands. *NJAS – Wag J Life Science* **57**(2):109–115 (2010).
44. ICIS, *ICIS Pricing: Prices for Chemicals*. [Online]. (2014). Available at: <https://www.icis.com/chemicals/channel-info-chemicals-a-z/> [Accessed: September 25 2014]
45. IEA, *Key World Energy Statistics*. International Energy Agency Saint-Just-La-Pendue, France, (2015).
46. Ftouni J, Muñoz-Murillo A, Goryachev A, Hofmann JP, Hensen EJM, Lu L *et al.*, ZrO_2 is preferred over TiO_2 as support for the Ru-catalyzed hydrogenation of levulinic acid to γ -valerolactone. *ACS Catalysis* **6**(8):5462–5472 (2016).

**Jonathan Moncada**

Jonathan Moncada is a PhD candidate at the Copernicus Institute of Sustainable Development, Utrecht University. He holds a bachelor degree and a master degree in chemical engineering. His research focuses on the ex ante assessment of novel technologies in biorefinery systems, with a special interest in bio-based chemicals.

**Ernst Worrell**

Ernst Worrell is professor of energy, resources and technological change at Utrecht University. He previously worked at Lawrence Berkeley National Laboratory and Princeton University. His research focuses on energy and material efficiency, and the role of technological change in the development of future energy and resource systems.

**Iris Vural Gürsel**

Iris Vural Gürsel is a postdoctoral researcher at the Copernicus Institute of Sustainable Development, Utrecht University. She holds a BSc degree in chemical engineering and MSc degree in engineering and technology management from Bogazici University. She obtained her PhD cum laude in chemical engineering at Eindhoven University of Technology.

**Andrea Ramírez**

Andrea Ramírez is professor of low carbon systems and technologies at Delft University of Technology. She holds a bachelor's degree in chemical engineering, a master's degree in human ecology, and a PhD in energy efficiency. She focuses on the sustainability assessment of novel bio-based chemicals and novel CO₂ capture and utilization technologies.

Appendix A: data inputs used in process modeling

Table A1 shows the set of reactions considered in the conversion of ethanol into butadiene modeled in Aspen Plus.

Table A2 shows the set of reactions considered in the conversion of levulinic acid into γ -valerolactone modeled in Aspen Plus. Table A3 shows the reactions considered in the production of caprolactam from GVL.

Table A1. Reactions modeled in butadiene production from ethanol. Case I: Reactor conditions: 425 °C, 1 bar. Data gathered from direct communication with experts from Delft University of Technology (TUDelft). Case II: Reactor conditions: 250 °C, 1 bar. Data gathered from Shylesh et al.,³³.

Reactions	Case I	Case II
	Conversion (%)	Conversion (%)
2 ethanol \rightarrow butadiene + hydrogen + 2 water	40.29	33.00
Ethanol \rightarrow ethylene + water	17.75	1.00
2 ethanol \rightarrow diethyl ether + water	9.26	0.00
2 ethanol \rightarrow acetaldehyde + hydrogen + ethylene + water	0.00	15.00
3 ethanol \rightarrow 2 propylene + 3 water	1.79	0.00
2 ethanol \rightarrow 1-butene + 2 water	2.23	1.00
2 ethanol \rightarrow isobutene + 2 water	0.95	0.00
2 ethanol \rightarrow 2-butene + 2 water	1.41	0.00
5 ethanol \rightarrow 2 pentene + 5 water	1.00	0.00
3 ethanol \rightarrow hexane + 3 water	0.00	0.00
2 ethanol \rightarrow 2-butanol + water	2.26	0.00
2 ethanol \rightarrow n-butanol + water	5.27	0.00
4 ethanol \rightarrow octanol + 3 water	1.75	0.00

Table A2. Reactions modeled in GVL production from levulinic acid. Reactor conditions: 150 °C, 30 H₂ bar, LA concentration 10% wt% in dioxane. Data gathered from Ftouni et al.,⁴⁶.

Reactions	Conversion (%)
Levulinic acid + hydrogen \rightarrow γ -valerolactone + water	100
γ -valerolactone + 2 hydrogen \rightarrow 1,4-pentanediol	4
1,4-pentanediol \rightarrow methyltetrahydrofuran + water	50

Table A3. Reactions modeled in the different steps for producing caprolactam based on data reported by Raoufmoghaddam *et al.*,¹⁵

Reactions	Case III	Case IV
	Conversion (%)	Conversion (%)
GVL Transesterification with methanol		
GVL + methanol \rightarrow 3-methyl pentenoate + water	72.75	72.75
GVL + methanol \rightarrow 4-methyl pentenoate + water	24.25	24.25
Aminolysis with ammonia		
3-methyl pentenoates + ammonia \rightarrow 3-pentenamides + methanol	100	100
4-methyl pentenoates + ammonia \rightarrow 4-pentenamides + methanol	96	96
Hydroformylation ^a		
3-Pentenamide + hydrogen \rightarrow valeramide	32.67	3.00
4-Pentenamide + hydrogen \rightarrow valeramide	32.67	3.00
3-pentenamide + carbon monoxide + hydrogen \rightarrow unsaturated caprolactam + water	56.43	90.00
4-pentenamide + carbon monoxide + hydrogen \rightarrow unsaturated caprolactam + water	56.43	90.00
3-pentenamide + carbon monoxide + hydrogen \rightarrow 4L (C ₆ H ₁₃ NO ₂)	0.99	1.00
4-pentenamide + carbon monoxide + hydrogen \rightarrow 4L (C ₆ H ₁₃ NO ₂)	0.99	1.00
3-pentenamide + carbon monoxide + hydrogen \rightarrow 1B (C ₆ H ₁₃ NO ₂)	8.91	6.00
4-pentenamide + carbon monoxide + hydrogen \rightarrow 1B(C ₆ H ₁₃ NO ₂)	8.91	6.00
Hydrogenation		
unsaturated caprolactam + H ₂ \rightarrow caprolactam	98.25	98.25

^a Catalyst: Rh/POP-xantphos.

Appendix B: additional data inputs and factors for the economic assessment

Table B1 displays the factors used for the estimation of capital investment. Table B2 shows the factors used for the estimation of operating costs.

Table B1. Factors used for the estimation of capital investment according to Peters *et al.*,³⁶

Purchased equipment	Percentage of purchased equipment ^a (%)
Direct costs	
Purchased equipment installation	39
Instrumentation and controls (installed)	26
Piping (installed)	31
Electrical systems (installed)	10
Buildings (including services)	29
Yard improvements	12
Service facilities (installed)	55
<i>Total direct</i>	<i>202</i>

Table B1. (Continued)

Indirect costs	
Engineering and supervision	32
Construction expenses	34
Legal expenses	4
Contractor's fee	19
Contingency	37
<i>Total indirect</i>	<i>126</i>
Working capital	75

^a Purchased equipment includes delivery costs (10%)**Table B2. Factors used for the estimation of additional features of operating costs Peters *et al.*,³⁶**

Category	Feature	Factor
Labor costs	Operating supervision	15% of operating labor
	Laboratory charges	15% of operating labor
Maintenance costs	Maintenance	6% of fix capital investment
	Operating supplies	15% of maintenance
Fixed and general costs	Taxes	2% of fix capital investment
	General	20% of labor, supervision and maintenance
Plant overhead	Plant overhead	60% of labor, supervision and maintenance