THESIS

FROM WASTE TO ENERGY: A TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ANALYSIS OF LIQUID BIOCHEMICAL PRODUCTION FROM WET WASTES THROUGH ENHANCED ANAEROBIC DIGESTION

Submitted by

Abdallah Soliman

Department of Mechanical Engineering

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Master's Committee:

Advisor: Jason C. Quinn

Kenneth Reardon
Bret Windom

ABSTRACT

FROM WASTE TO ENERGY: A TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ANALYSIS OF LIQUID BIOCHEMICAL PRODUCTION FROM WET WASTES THROUGH ENHANCED ANAEROBIC DIGESTION

Wet wastes such as manure and food wastes present problems due to disposal costs and environmental impacts. Low value products and methane leaks limit the sustainability and viability of current anaerobic digestion for treatment of wet waste. Electrochemically enhanced conversion of wet wastes diverts carbon from low-value methane into volatile fatty acids that are subsequently upgraded to improve anaerobic digestion sustainability and generate biochemicals which are seamlessly compatible with the current infrastructure. A chain elongation pathway and a bioconversion pathway are used to produce caproic acid and n-butanol, respectively. Techno-economic analysis and life cycle assessment are used to demonstrate the economic and environmental viability of the technology. The economic analysis generates market competitive minimum selling prices of $1.05 per kg for the caproic acid pathway and $2.25 per kg for the n-butanol pathway. The baseline environmental analysis yields an environmentally unfavorable GWP of 72.1 g CO_2-eq·$MJ_{caproic\ acid}^{-1}$ for the chain elongation pathway whereas the GWP of the bioconversion pathway (24.0 g CO_2-eq·$MJ_{n\text{-}butanol}^{-1}$) qualifies it as a renewable fuel under the RFS program. Using scenario and sensitivity analyses, critical research areas were highlighted to guide future work and improve the performance and sustainability of the technology.

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TABLE OF CONTENTS

1. INTRODUCTION

The storage of manure and the landfilling of food waste (FW) results in considerable emissions of methane (CH_4), ammonia (NH_3) and nitrous oxide (N_2O). Two of the gases, CH_4 and N_2O, are greenhouse gases (GHG) that contribute to global warming with a 100-year global warming potential (GWP) of 28 and 265 carbon dioxide-equivalent (CO_2-eq) emissions, respectively [1]. Whereas NH_3 contributes to acidification and eutrophication which lead to a decrease in biodiversity and contribute to climate change [2]–[4]. Anaerobic digestion (AD) is currently a well-established commercial technology used to treat these wet wastes and produce biogas that can be used as a renewable energy source. However, current AD technologies have many limitations including, methane leaks and the production of economically unattractive products. Methane, the primary component of biogas has been identified as a low value product [5]. Moreover, economically, biogas plants are not justified and depend greatly on availability of tax incentives, feed in tariffs, and support from the government [6]. A potential solution is the diversion of the carbon conversion in AD from low value methane to more economically attractive products using up-cycling of volatile fatty acids (VFAs).

VFAs are short carboxylic acids produced during the acidogenesis step of AD which falls before methanogenesis. Electrochemically arrested methanogenesis diverts production from CH_4 to VFAs [7], [8]. VFAs mainly include acetic acid, propionic acid, and butyric acid [9] and are important building blocks for high value chemicals such as long chain acids and alcohols. Chain elongation is a biotechnological process where microorganisms convert VFAs and an electron donor into more valuable medium chain fatty acids. According to recent research studies, VFAs can be upgraded using ethanol and electro-elongation to produce caproic acid, a hydrocarbon precursor [10]. Other research studies investigated another biotechnical process, bioconversion, where microorganisms use hydrogen as an electron donor to upgrade VFAs to C3-C4 higher alcohols, mainly n-butanol, ethanol and propanol which can be upgraded to jet fuel or used as a gasoline blend stock [11]. Hence, the upgrading of VFAs could enhance AD operations by producing high value products. Recent research has focused on increasing VFA production, removal of VFAs using Electrodialysis (ED) and upgrading VFAs, and has yielded positive results. However, the majority of the research has been executed on a laboratory scale failing to represent a real-life scenario [12]–[16]. To understand the economic and environmental implications related to commercial scale production of biochemicals from AD of wet wastes, experimental data must be coupled with Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA).

Few studies have focused on the economics of VFA production from AD [17], [18] and fewer have evaluated VFA upgrading. Those that do are limited by a narrow scope excluding steps such as digestate disposal and use, VFA extraction, and the effect of pre-treatment. A comprehensive sustainability analysis of VFA production from AD was published by Veluswamy et al. [5]. Although this publication is thorough, it focuses primarily on VFA production from AD and does not include the upgrading of VFAs and the environmental impact of VFA production. An environmental life cycle assessment evaluated the production of caproic acid from mixed organic waste in Chen et al. [19] but failed to account for digestate fertilizer substitution. Digestate, the other main product of AD, has a large potential for global warming savings from fertilizer substitution through the use of its nitrogen (N) and phosphorus (P) content [20]. Thus, digestate end use must be accounted for to understand the full impact of AD. Another comprehensive sustainability analysis evaluated the production of aviation fuel from wet-waste derived VFAs [21]. Although the LCA in that study achieved negative carbon intensity it also failed to capture the impact of digestate on both TEA and LCA.

To the best of the authors' knowledge, no literature exists that applies a coupled economic and environmental impact methodology to caproic acid and n-butanol production from AD. In this study the production of caproic acid and n-butanol from wet wastes using chain elongation and bioconversion, respectively, is evaluated. To predict the sustainability and performance of the system, an engineering sub-process model based on mass and energy balance validated with literature performance data is used to inform TEA and LCA. The sub-processes used to produce biochemicals in this study included AD, ED, a chain elongation reactor, and a bioconversion reactor. A centrifuge decanter, a stripping column, an absorbing column, and a nitrification reactor are used in this study to model the handling and disposal of digestate. In total two pathways are evaluated, a chain elongation pathway producing caproic acid and a bioconversion pathway producing n-butanol as a primary product. Results and discussion focus on system performance, and sensitivity and scenario analysis to drive the technology towards sustainability.

2. MATERIALS AND METHODS

The methodology used to compare different pathways consisted of 3 steps: 1) Developing and validating a sub-process engineering model to serve as the foundation for evaluation of the process and track mass and energy. 2) Evaluating the economic and environmental feasibility of producing caproic acid and n-butanol from AD by generating a minimum selling price (MSP) and GWP using TEA and LCA, respectively. 3) Identifying critical research areas via sensitivity analysis, multiple scenario analysis, and stochastic modeling. All processes and modeling were developed in Microsoft Excel using Virtual Basic for Applications (VBA) to execute different analyses including economic, environmental, sensitivity, scenario and Monte Carlo.

2.1. Case study

The processing of manure and FW began by modeling the AD reactor (100) where VFAs, carbon dioxide (CO_2) and digestate were produced. The feedstock was homogenized to reduce its solid content using water and sodium hydroxide (NaOH) was used to neutralize and control pH inside the AD reactor. The VFAs were then recovered by ED (200) to produce a high titer VFA stream that was fed to the upgrading reactors. Next, two upgrading pathways were considered. The first was chain elongation (500) where acetate, butyrate, and ethanol were used to produce caproic acid. In the second pathway all VFAs were fed to a bioconversion reactor (600) to produce alcohols using hydrogen as an electron donor. The system assumed the absence of land to apply digestate on site and the need for solid-liquid separation (SLS) of digestate to facilitate transport to other lands for field application. Using a centrifuge decanter (300) digestate was separated to a solid and liquid fraction. The liquid fraction was treated to reduce its ammonia toxicity using a stripping column (410), an absorbing column (420) and a nitrification reactor

(430). Cumulatively, these operations make up the downstream processing facility and are illustrated in Figure 1. The system boundary shown in Figure 1, includes the processes of anaerobic digestion of feedstock, separation of VFAs using ED, upgrading of VFAs using the two different pathways (chain elongation and bioconversion), SLS of digestate and, the treatment of liquid digestate to remove N.

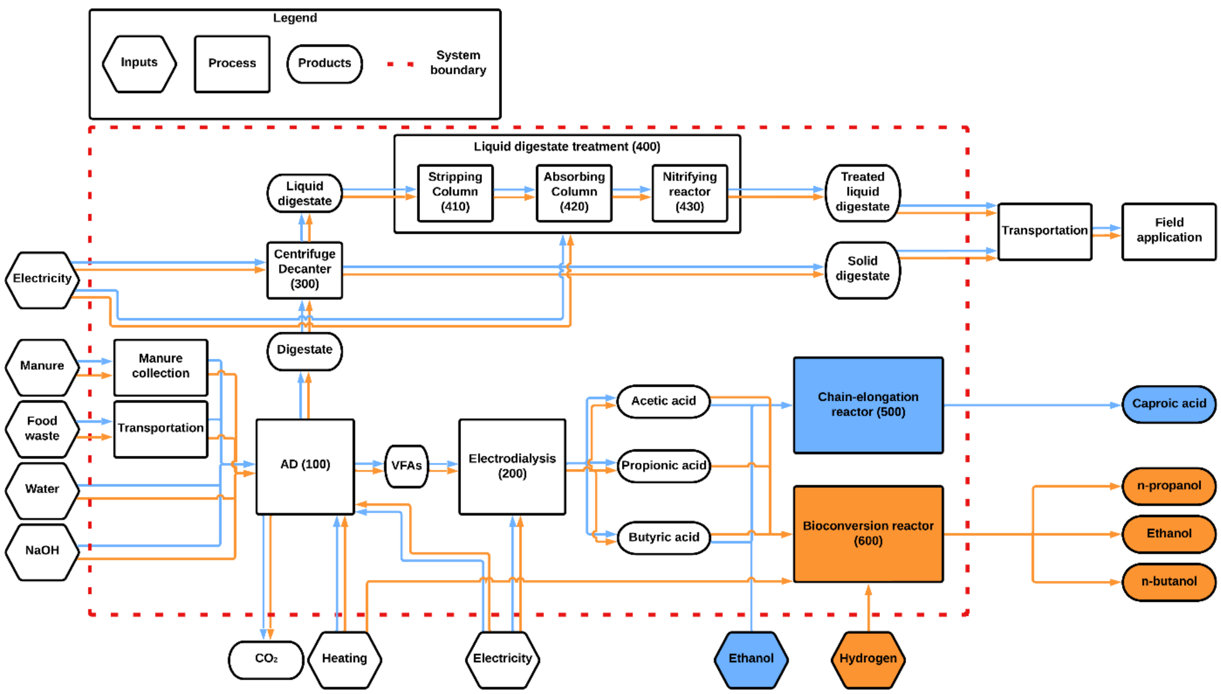


Figure 1: System flow diagram illustrating the baseline pathways evaluated. The chain elongation pathway is illustrated in blue and the bioconversion pathway is illustrated in orange. The baseline scenarios assume the use of manure and food waste as a feedstock, feedstock homogenization using water in the AD, pH control with NaOH in the AD, electrodialysis to extract VFAs, SLS of digestate using a centrifuge decanter and treatment of liquid digestate before land application. Caproic acid is produced from chain elongation of VFAs. Ethanol, n-butanol and n-propanol are produced from the bioconversion of VFAs. (VFAs: Volatile Fatty Acids; SLS: Solid-Liquid Separation; AD: Anaerobic Digestion)

The proposed system design assumed the use of 20% of total food waste generated in Denver, CO (167,114 MT·year^{-1}) [22] and manure generated from the Gilcrest feedlot (69,000-head feed yard) [23] in LaSalle, CO. Beef cattle were expected to produce 52.16 kg·head^{-1}·day^{-1}

[24] of untreated fresh manure with total solid (TS) percentage of 13.6±1.1% [25] collected at a cost of 120.5 $\$\cdot cow^{-1}\cdot year^{-1}$ [26]. The cost of collecting manure is related to the operating costs of collecting machinery. A 10 $\$\cdot MT\ FW^{-1}$ tipping fee was charged to accept food waste compared to the 17-30 $\$\cdot ton^{-1}$ range of tipping fees generally paid to dispose of Municipal Solid Waste (MSW) in the landfill [27]. FW was assumed to be transported from Denver to LaSalle where the plant was assumed to be located for 0.18$\$\cdot ton^{-1}\cdot mile^{-1}$, assuming a 100 miles round trip. A tipping fee was received for FW and not for manure because manure can be land applied by farmers at zero cost [28].

2.2. Engineering process model development

The engineering process model was developed to accurately capture the mass and energy requirements of each sub-process and to provide the foundation for TEA and LCA work. The baseline inputs provided in Table 1 were used to define the performance of each sub-process and the overall system.

Table 1: Summary of baseline input parameters. The parameters are used to define mass and energy flows to inform the TEA and LCA of production of caproic acid and n-butanol using chain elongation and bioconversion, respectively. The parameters are also used to define production and handling of digestate. (HRT: Hydraulic Retention Time; TS: Total Solids; VS: Volatile Solids; VFA: Volatile Fatty Acid)

Parameters	Values		Reference
Anaerobic digestion (100)			
Feedstock:	***Food Waste***	***Manure***	
Operating time [$hrs\cdot year^{-1}$]	8,000	8,000	[29]
Feedstock flow rate [$kg\cdot hr^{-1}$]	3,815	149,960	[22], [23]
HRT [days]	10	10	[5]
Digester temperature [ºC]	40	40	[29]
Digestate yield [% of feedstock volume]	90%	90%	[30]
TS%	40.5%	13.6%	[25], [31]
VS%	98.6%	85.3%	[25], [31]
VFA yield [$g\ VFA\cdot g\ TS^{-1}$]	0.63	0.56	[32], [33]
Carbon%	47.8%	45.4%	[34], [35]
Nitrogen%	5.2%	1.0%	[34], [35]
Phosphorus %	0.5%	0.2%	[25], [36]
Ash content	7.7%	31.8%	[36], [37]
Electro-dialysis (200)			

Acetate % recovery	83.0%	83.0%	[38]
Propionate % recovery	87.0%	83.0%	[38]
Butyrate % recovery	66.0%	83.0%	[38]
Energy consumption [kWh·kg VFA^{-1}]	5.43	5.43	[38]
Centrifuge decanter (300)			
Digestate:	***Solid***	***Liquid***	
C	70%	30%	[39]
TS	86%	14%	[39]
Water	6%	94%	[39]
TN	25%	75%	[39]
TP	78%	22%	[39]
Liquid digestate treatment (400)			
Stripping column (410)			
pH	10.5		[40]
Ammonia stripping	93%		[40]
Temperature [ºC]	50		[40]
Molar ratio [Liquid·$Vapor^{-1}$]	0.66		[40]
Absorbing column (420)			
Ammonia absorption	70%		[40]
Nitrifying reactor (430)			
HRT [hrs]	12		[41]
Energy consumption [kWh·kg N^{-1}]	3.54		[42]
Upgrading pathway			
Chain-elongation (500)			
HRT [days]	20		[43]
Ethanol:acetate	2.76		[43]
Ethanol:butyrate	0.77		[43]
Caproic acid carbon conversion from VFAs and ethanol	0.51		[43]
Bioconversion (600)			
HRT [days]	25		[11]
Ethanol carbon conversion from acetate	0.42		[11]
n-propanol carbon conversion from propionate	0.38		[11]
n-butanol carbon conversion from butyrate	0.55		[11]
Reactor temperature [ºC]	30		[11]

2.2.1. Anaerobic digester (100)

A continuous stirred tank reactor (CSTR), the most usual reactor type for AD, was used to model the anaerobic digester [44]. To determine the size of the digester the following formula was used:

$$V_D = [V_m + V_{fw} + V_w] * HRT (1)$$

where V_D is the digester volume in m^3, V_m is the manure volume in $m^3 \cdot day^{-1}$, V_{fw} is the food waste volume in $m^3 \cdot day^{-1}$, V_w is the water volume in $m^3 \cdot day^{-1}$ and hydraulic retention time (HRT) is in days. The water volume used to homogenize feedstock in the digester was estimated by calculating the water required to reach a target 9.5 TS% [45]. A 10 day HRT was assumed [5]. VFA yields of 0.56 and 0.63 kg VFA·kg TS^{-1} fed were used for manure and FW, respectively. Acetate, propionate, and butyrate were assumed to be the only VFAs produced from AD with a VFA profile favoring the production of acetate dependent on the feedstock used. Accordingly, VFA composition were estimated to be 56.7% acetate and 11.5% propionate and 31.8% butyrate [46]. Furthermore, the model assumed no methane production and a CO_2 yield of 214.56 mL·g volatile $solids^{-1}$ (VS) [47]. Using equation (1), the size of the reactor was determined and used to estimate capital expenditure (CAPEX) of the AD CSTR presented in Table 2. To estimate the operational expenditure (OPEX) associated with AD the following assumptions were made. The water was assumed to cost 1.23 \$·MT^{-1} [48]. The heat demand of the reactor was calculated assuming mesophilic digestion at 40ºC and formulas from Akbulut [29]. Finally, the model considered that for every mole of VFA produced a mole of H^+ was produced. Accordingly, the system required pH control using NaOH, which was assumed to cost 429 \$·MT^{-1} [49].

2.2.2. Electrodialysis (200)

Electrodialysis (ED) efficiently extracts VFAs for upgrading from a complex AD liquid stream producing a high titer VFA stream. An electric field facilitates the movement of ions across a semipermeable membrane. ED was modeled because it is a membrane separation technology that is already in use in many large-scale chemical processes [38], [50], [51]. ED processes have successfully demonstrated high VFA recovery (up to 99%) in previous studies but the model in this study uses conservative assumptions as shown in Table 1 [38]. The CAPEX of ED presented in Table 2 was estimated using two membranes each with an area of 13,165 m^2 scaled from Pan et al. [38], a 10 year lifetime and a cost of 320\$·m^{-2} [52]. Moreover, a 5.43 kWh·kg VFA^{-1} energy cost was used to model OPEX of ED [38].

2.2.3. Treatment of digestate (300/400)

Digestate is the residual product of AD and is usually used as a fertilizer. Digestate is either land applied directly as fertilizer for its Nitrogen (N) and Phosphorus(P) content or is treated using SLS before it is applied to a field [53]. The model assumed that digestate accounted for 90% of the feedstock volume [30], and had a dry matter content of 2.8% [39] and a density of 993 $kg \cdot m^{-3}$ [54]. It was considered that all N and P available in the feedstock was recovered in digestate after AD given that only organic matter is converted to VFAs and N and P are not consumed during the process [55]. The high concentrations of N, solids, and undigested carbon can be a potential oversupply for local farmland needs [56]. Accordingly, the baseline assumption was that digestate must be separated into solid and liquid to facilitate its transportation to different land areas (see Figure 1). The solid fraction of digestate can be field applied directly as organic fertilizer. Although the liquid fraction can be used to irrigate fields, its high N concentration limit its direct application to the soil. Therefore, liquid digestate must be treated further to remove N and reduce ammonia toxicity [44]. The model used a centrifuge decanter with separation efficiencies specified in Table 1 to achieve SLS of digestate [57]. Moreover, this model assumed that liquid digestate was treated using the method and assumptions used in Alhelal et al. [40] where, a stripping column, an absorption column and a nitrifying reactor were used to reduce ammonia toxicity of digestate (see Table 1 for parameters). The N and P in digestate are potential substitutes for the fertilizers urea and triple phosphate, respectively. To determine the mass of synthetic fertilizer that can be replaced from N and P in digestate the following formula was used:

$$\text{Fertilizer replaced} = \text{chemical element applied} * \text{substitutability factor} * \frac{\text{MW fertilizer}}{\text{MW chemical element}} \quad (2)$$

where chemical element applied is N or P and fertilizer is urea or triple phosphate, respectively. Plant availability is how much N or P is available for crop uptake. Given that bioavailability of nutrients in AD digestate is not the same as synthetic fertilizer a substitutability factor of 60% was assumed [58]. The CAPEX associated with the decanter centrifuge, stripping and absorbing columns are presented in Table 2. Finally, the nitrifying reactor was assumed to be a CSTR with its CAPEX shown in Table 2. To accurately capture the OPEX for digestate treatment an electricity demand of 4 $kWh \cdot m^{-3}$ [57] for the decanter centrifuge and an energy cost of 3.54 $kWh \cdot kg\ N^{-1}$ for the denitrification process [42] were added to the total OPEX of the system. The revenue generated from selling N and P based digestate fertilizers corresponding respectively to urea and triple phosphate was calculated using the assumptions that these fertilizers were sold for their 10-year average market prices of 298 $\$ \cdot MT^{-1}$ and 364 $\$ \cdot MT^{-1}$, respectively [59], [60].

2.2.4. Chain-elongation (500)

Caproic acid is a valuable industrial product and a chemical precursor. Thus, the upgrading of VFAs to caproic acid becomes a very attractive pathway following AD [61]–[65]. Clostridium kluyveri is an anaerobic bacterium capable of producing caproic acid by chain elongating ethanol and short chain fatty acids through a reaction known as reversed β-oxidation [66]. The ethanol required for the chain elongation of VFAs was calculated based upon an ethanol:acetate ratio of 2.76 g $ethanol \cdot g\ acetate^{-1}$ and ethanol:butyrate ratio of 0.77 g $ethanol \cdot g\ butyrate^{-1}$[43]. According to research studies, yield can be increased using serial reactors [67]–[69]. Therefore, the chain elongation reactor was modeled as four serial CSTRs with unconverted acetate, butyrate and ethanol from the previous reactor feeding the subsequent reactor. Similar to the method used in section 2.2.1. Anaerobic digester (100), the volume of each of the chain elongation CSTRs was calculated using a 20 days HRT and the volumetric flow rates of butyrate, acetate and ethanol, assuming caproic acid is removed after each reactor [43]. The production of caproic acid from each reactor was estimated using a carbon conversion yield of 0.51 per acetate, butyrate and ethanol [43]. All reactors were operated with the same parameters and the caproic acid yields from all reactors were summed to determine the final caproic acid yield of the system. The CAPEX of the four chain elongation reactors was estimated using the reactor volumes and is presented in Table 2. The OPEX of chain elongation was captured by applying a ten-year average cost of 578$$\cdot$$MT$_{ethanol}^{-1}$ to estimate the yearly cost of providing ethanol for the system [70].

2.2.5. Bioconversion (600)

Long chain alcohols such as butanol are considered valuable due to their higher energy density [71]. Using biosynthesis, acetate, propionate and butyrate can be upgraded with the presence of an electron donor, to ethanol, propanol and n-butanol, respectively [11], [72]. The model used hydrogen as the electron donor and assumed that 2 moles of hydrogen were required per mole of VFA. The alcohols yields from the bioconversion reactor were determined using a carbon conversion yield of 86.8% for ethanol from acetate, 37.8% for propanol from propionate and 55.0% for n-butanol from butyrate [11]. Conversely to the chain elongation pathway, only three serial bioconversion CSTRs were used to increase the yield from bioconversion. Moreover, in this pathway the CSTRs had a HRT of 25 days and were heated to 30ºC. The CAPEX associated to the serial CSTRs is presented in Table 2 and was calculated based on reactor volumes that were estimated using the volumetric flow rate of VFAs and the HRT. The OPEX included the cost of hydrogen procurement assumed to be 1.39 $\$\cdot kg^{-1}$ [73] and similarly to the AD reactor, heating energy was determined using the assumptions and formulas used to calculate a reactor heat demand in Akbulut [29]. The major product from this pathway was considered to be n-butanol with ethanol and n-propanol being co-products that were assumed to be sold for their 10-year average market prices of 578$$\cdot$MT^{-1} and 991 $\$\cdot$MT^{-1}, respectively [70], [74], [75].

2.3. Techno-economic analysis

2.3.1. Discounted cash flow rate of return

The economic viability of the two production pathways were evaluated using TEA. The TEA used a 20-year Discounted Cash Flow Rate of Return (DCFROR) model to determine the MSP for the caproic acid produced from chain elongation pathway and the n-butanol produced in the bioconversion pathway. The model assumed a 10% Internal Rate of Return (IRR), a 35% tax rate, a 3-year construction period and a facility production capacity of 50% during the first year. A 7 years Modified Accelerated Cost Recovery System (MACRS) depreciation schedule consistent with Cruce and Quinn [76] was applied to the CAPEX and working capital was assumed to be 5% of total CAPEX. The TEA used an interest rate of 8%, a loan term of 10 years, and a 40% equity. Using the total OPEX, CAPEX from the different sub-processes, the yearly production of caproic acid or n-butanol, and yearly co-product revenue the MSP price was estimated such that the production facility had a net present value (NPV) of zero. The MSPs were expressed in $\$\cdot$kg^{-1} of caproic acid or n-butanol.

2.3.2. Capital and operational costs

Capital costs for each sub-process were scaled using a 0.6 scaling factor [77]. CAPEX was adjusted to a cost year of 2018 using the respective indices listed in the Chemical Engineering Plant Cost Index. The total investment cost associated with the case study is detailed in Table 2 (see the supplementary materials for additional info).

Table 2. The investment cost of sub-processes for caproic acid and n-butanol production from VFAs produced in anaerobic digestion of wet wastes.

Equipment name	Capacity	Units	Installed cost in 2018	Reference
Anaerobic digester	50,448	m^3	$3,556,674 [a, b]	[78], [79]
Electrodialysis	13,165	m^2	$12,877,251 [a, b]	[52]
Decanter Centrifuge	96	$m^3\cdot hr^{-1}$	$332,046 [a, b]	[80]
Stripping Column	7,367	kmol air$\cdot hr^{-1}$	$2,278,775 [a, b]	[81]
Absorbing Column	7,367	kmol air$\cdot hr^{-1}$	$2,740,227 [a, b]	[81]
Nitrifier Reactor	2,609	m^3	$466,217 [a, b]	[79]
Chain elongation reactor 1	10,500	m^3	$21,889,993 [a]	[82]
Chain elongation reactor 2	5,305	m^3	$11,062,582 [a]	[82]
Chain elongation reactor 3	1,892	m^3	$3,956,623 [a]	[82]
Chain elongation reactor 4	675	m^3	$1,406,775 [a]	[82]
Bioconversion reactor 1	4,002	m^3	$8,356,872 [b]	[82]
Bioconversion reactor 2	1,608	m^3	$3,356,018 [b]	[82]
Bioconversion reactor 3	466	m^3	$973,724 [b]	[82]

As mentioned in the previous sections operational costs included yearly feedstock acquisition, water costs to homogenize feedstock, ethanol and hydrogen procurement, base acquisition for pH control, reactors' heating, electricity and energy demand for each sub-process, water for feedstock homogenization acquisition, maintenance, and labor costs. Electricity and heating costs were assumed to be 0.0695 $\$\cdot kWh^{-1}$ and 0.0198 $\$\cdot kWh^{-1}$, respectively [83], [84]. Annual maintenance was assumed to be 3% of total CAPEX [77] and labor was calculated using the method provided in Robbins et al. [85]. Labor is calculated based on the number of process steps. This model assumed a total of 5 process steps representing AD, ED, upgrading reactor, SLS of digestate and treatment of liquid digestate.

The costs of co-products such as n-propanol and market price of n-butanol were assumed to be correlated to the price of crude oil. Accordingly, the ten-year average prices were determined by extrapolation using the ten-year cost trends of crude oil [75].

[a] CAPEX specific to the chain elongation pathway.

[b] CAPEX specific to the bioconversion pathway.

2.4. Life cycle assessment methods

The LCA quantifies the environmental impacts and viability of the cradle to gate production of VFAs from wet waste and upgrading them to displace petroleum-based products. The system boundaries of the LCA were consistent with the TEA and included emissions associated with the feedstock procurement, electricity, heating, and plant construction. The material and energy results from the process model were used as a foundation for the LCA. These inputs were coupled with their associated life cycle inventories (LCI) representing their emissions. LCI were primarily obtained from ecoinvent in openLCA using the U.S. Environmental Protection Agency's recommended Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) [86], [87]. LCI data unavailable in ecoinvent was retrieved from literature. The 100-year GWP was calculated for both caproic acid and n-butanol on an energy basis in g CO_2-eq·MJ^{-1} to use energy allocation. The total GWP was estimated by combining emissions from the various mass and energy flows obtained from the engineering sub-process model. The GHG emissions associated with each flow were calculated using the following energy allocation formula:

$$\mathrm{GWP}_{\mathrm{flow\ x}} = \frac{\mathrm{P_x LCI_x}}{\mathrm{P_{products}\, LHV_{products}}} * \frac{\mathrm{P_{primary\ product}\, LHV_{primary\ product}}}{\mathrm{P_{products}\, LHV_{products}}} \quad (3)$$

where $\mathrm{GWP}_{\mathrm{flow\ x}}$ are the emissions associated with flow x in kg CO_2-eq·MJ^{-1}, P is the yearly production in production unit·year^{-1}, LCI is the life cycle inventory in kg CO_2-eq·production unit^{-1}, and LHV is the low heating value in MJ·kg^{-1}. The low heating values used for caproic acid, ethanol, n-propanol and n-butanol were 30.06 MJ·kg^{-1}, 26.7 MJ·kg^{-1}, 30.68 MJ·kg^{-1} and 34.4 MJ·kg^{-1}, respectively [88]–[90].

Avoided emissions from FW landfilling, manure land application, manure storage, produced N and P based digestate fertilizers were applied as credits, equal in value to the emissions of the processes being displaced, and subtracted to the cumulative emissions associated with the production of caproic acid or n-butanol from wet wastes. Specific to the bioconversion pathway, co-products with an associated energy value such as ethanol and n-propanol are credited by energy allocation.

The LCI of FW landfilling and transportation, manure land application, collection, transportation, and storage, and digestate storage were retrieved from literature due to the lack of data in ecoinvent. The GWP of FW landfilling was estimated to be 2.969 kg CO2-eq·kg FW^{-1} [3]. FW transport was consistent with assumptions made for TEA (see 2.1. Case study) and was estimated to be 0.1894 kg CO_2-eq·kg FW^{-1} based on the assumption that 70% of the distance from Denver to LaSalle was a nonstop driving and 30% of it was a stop/drive [91]. The model assumed emissions of 0.0164 kg CO_2-eq·kg^{-1}, 0.0027 kg CO_2-eq·kg^{-1}, 0.0014 kg CO_2-eq·kg^{-1}, and 0.0838 kg CO_2-eq·kg^{-1} for manure land application, collection, transportation, and storage, respectively. The manure was assumed to have been applied by injection after being stored for 6 months with no agitation or crust. It was also assumed to be collected by skid steer and alley scrapper and transported via pump and tanker [4]. The digestate was assumed to be stored in an open tank, hence emitting 0.1309 kg CO_2-eq·kg $digestate^{-1}$ [92]. The production of bioethanol used during chain elongation was assumed to be corn based which is considered to be the main ethanol source in the US [93]. The emissions associated with the transport and land application of digestate following its SLS were left outside the system boundary in this study because the emissions associated with digestate field application were not particularly well understood.

2.5. Sensitivity, scenario and Monte Carlo analyses

A single point sensitivity analysis was performed on 132 model inputs, to determine critical research areas, high impact inputs, and verify the model. Each input was adjusted by ±20% from its baseline value with MSP and GWP recorded. The information from the sensitivity analysis was used to determine the 10 inputs with the highest impact on MSP and GWP to help generate scenarios that could be investigated to improve the performance of the system economically and environmentally.

Monte Carlo was used to understand the certainty of the results with the top 5 sensitive variables determined from the sensitivity analyses assigned distributions from literature as described in Table 3. More details on the distributions are in the supplementary materials. Each of the 5 high impact inputs were assigned a random value within their distributions for each of the 10,000 iterations performed. The Monte Carlo analysis generated a probability distribution, mean, minimum, maximum, median, and 90% confidence intervals for the MSPs and GWPs of both pathways.

Table 3: Distributions used for the Monte Carlo analysis (10,000 iterations) of the minimum selling price and global warming potential for caproic acid and n-butanol production from VFAs produced in anaerobic digestion of wet wastes. (TS: Total Solids; VFA: Volatile Fatty Acid)

Parameter	Max	Mean	Min	Standard deviation	Distribution type	Source
Operating time [$hrs \cdot year^{-1}$]	8760	8380	8000	NA	Uniform	[29]
Manure TS%	NA	13.6%	NA	1.19%	Normal	[25]
Manure VFA yield [$g\ VFA \cdot g\ TS^{-1}$]	NA	0.56	NA	0.06	Normal	[33]
Acetate percent in VFA	NA	56.7%	NA	1.1%	Normal	[46]
Butyrate percent in VFA	NA	31.8%	NA	1.1%	Normal	[46]
Percent VFA recovery	100%	78.1%	NA	10.6%	Normal	[38]
Caproic acid yield	NA	50.9%	NA		No Distribution	[43]
Ethanol:acetate carbon conversion yield	100%	86.8%	NA	13.5%	Normal	[11]
n-butanol:butyrate carbon conversion yield	NA	55.0%	NA	7.8%	Normal	[11]

Ethanol price [$\$\cdot MT^{-1}$]	See P-table in SI	Histogram	[70]

3. RESULTS AND DISCUSSION

An engineering process model was developed and used to evaluate the economic and environmental performance of two different biochemical production pathways based on an anaerobic digester tailored to the production of VFAs. The produced VFAs were upgraded using two unique pathways based on either chain elongation or bioconversion, which produce caproic acid and n-butanol, respectively. Results for each pathway include MSPs and GWPs.

3.1. Techno-economic analysis

Total CAPEX and OPEX combined with system performance were used to determine the MSPs for both upgrading pathways. Sensitivity and scenario analyses were used to determine and investigate high impact variables affecting the MSPs.

3.1.1. Baseline minimum selling price

The baseline pathways illustrated in Figure 1, are the basis for comparison of all the following scenarios. The model generates MSPs of $1.05 per kg caproic acid and $2.25 per kg n-butanol for the chain elongation and bioconversion pathways, respectively.

3.1.1.1. Chain elongation

The baseline MSP of caproic acid is divided into major cost contributors, OPEX, CAPEX, taxes and co-products in Figure 2A, with the figure including other scenario results to be discussed in section 3.1.2. The OPEX (93.9%) represents the largest contributor to the MSP followed by the CAPEX (5.6%) and taxes (1.7%) which is consistent with a previous study on anaerobic digestion of manure [94].

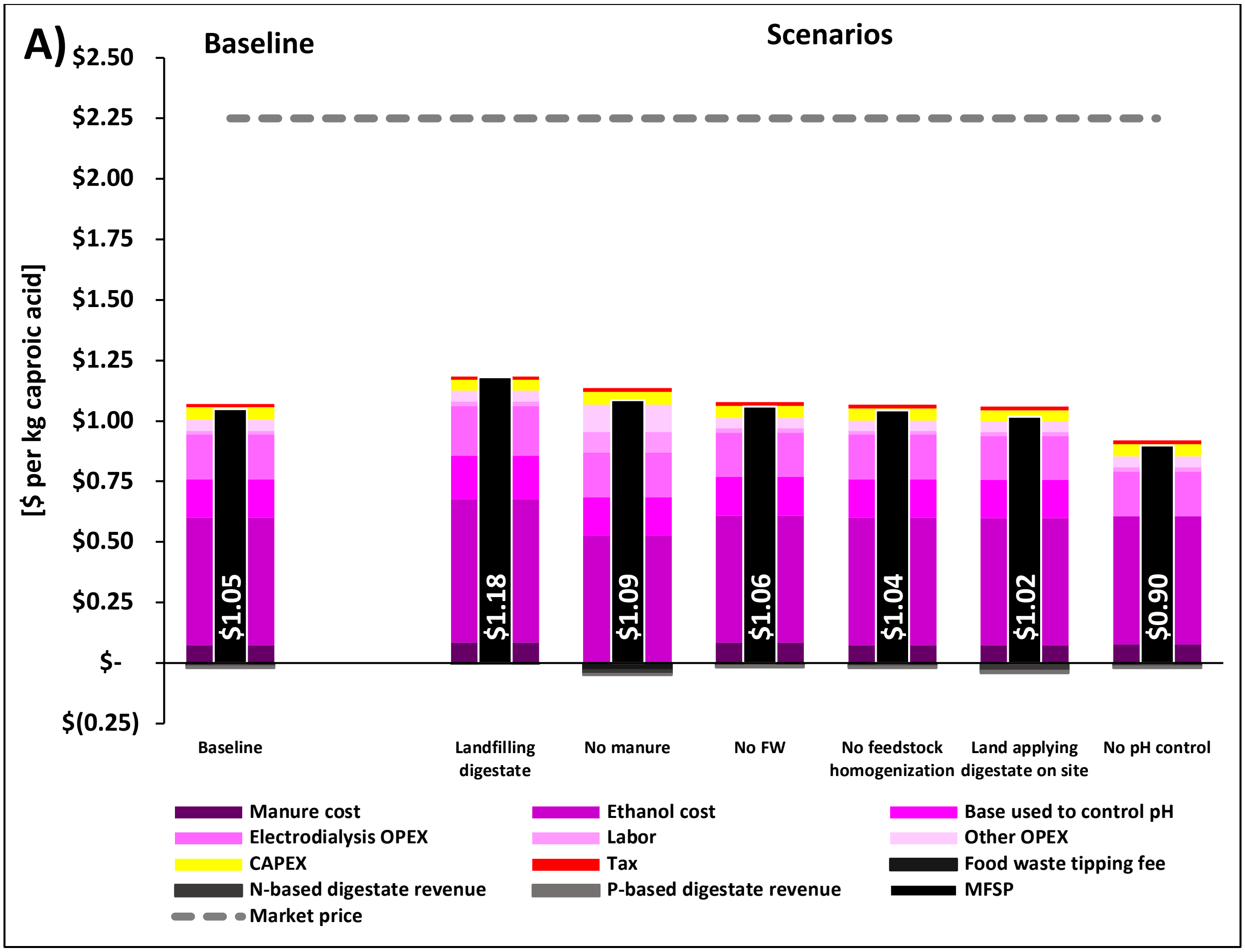
The OPEX ($112 M) in the chain elongation pathway is dominated by the ethanol procurement cost as shown in Figure 2A. The ethanol has a large impact on OPEX due to the large volumes required for VFAs chain elongation. Moreover, the ethanol high demand increases the volume of the chain elongation reactors considerably which increases the CAPEX. Similarly, ED is a large contributor to both OPEX and CAPEX due to its high energy demand and the capital costs of membranes. Although ED is subject to high operational and capital costs previous research has shown the high VFA recovery offsets these costs [95], [96]. The base procurement cost is also one of the main contributors to OPEX because it is directly correlated to the high production of VFAs and is used to neutralize pH. The other operational costs presented in Figure 2A include heating, electricity, labor, maintenance, food waste transportation cost, energy requirements of the decanter centrifuge, and water cost (specific contributions are detailed in supplementary materials).

The carbon conversion efficiency of wastes to VFAs is in AD 56.7% which is higher than the carbon conversion efficiency achieved for waste to biogas in conventional AD (9.4%-30%) [94], [97], [98]. Specific to this pathway, more carbon is added in the form of ethanol for VFA chain elongation which accounts for 48.7% of the total carbon fed to the system. Using serial chain elongation reactors each with carbon conversion efficiency of 50.5% increases carbon recovery and achieves a 97.8% total carbon conversion yield in chain elongation. Based on this, the caproic acid MSP is based on a total carbon conversion efficiency of 67.0% (see Sankey diagram in the supplementary material) and yearly caproic acid production of 117,443 MT.

3.1.1.2. Bioconversion

Similar to the chain elongation pathway, OPEX ($55.1 M) is the largest contributor to the n-butanol MSP. ED and pH control are large contributors to OPEX because of the high energy demand of ED and high base demand to neutralize pH, respectively (see Figure 2B). The other operational costs include hydrogen cost, heating, electricity for AD, labor, maintenance, food waste transportation cost, energy requirements of the decanter centrifuge and water cost, and are detailed in the supplementary materials. Specific to the bioconversion pathway, co-product credits ($1.87 per kg n-butanol) offset the total production costs ($4.13 per kg n-butanol) considerably, as observed in Figure 2B. The high contribution of ethanol sales is correlated to the high ethanol production in the bioconversion reactor which is attributed to the VFA profile dominated by acetate the precursor of ethanol in bioconversion.

Consistent with the chain elongation pathway, a 56.7% carbon conversion efficiency is achieved in AD. The 69.6% carbon conversion efficiency in each serial bioconversion reactor achieves a 96.6% total carbon conversion efficiency for bioconversion. Therefore, the n-butanol MSP is based on a total carbon conversion efficiency of 42.3% and a yearly n-butanol production of 15,882 MT.


A)
Baseline
Scenarios
[$ per kg caproic acid]
$2.50
$2.25
$2.00
$1.75
$1.50
$1.25
$1.00
$0.75
$0.50
$0.25
$-
$(0.25)
$1.05
$1.18
$1.09
$1.06
$1.04
$1.02
$0.90
Baseline
Landfilling digestate
No manure
No FW
No feedstock homogenization
Land applying digestate on site
No pH control
Manure cost
Ethanol cost
Base used to control pH
Electrodialysis OPEX
Labor
Other OPEX
CAPEX
Tax
Food waste tipping fee
N-based digestate revenue
P-based digestate revenue
MFSP
Market price

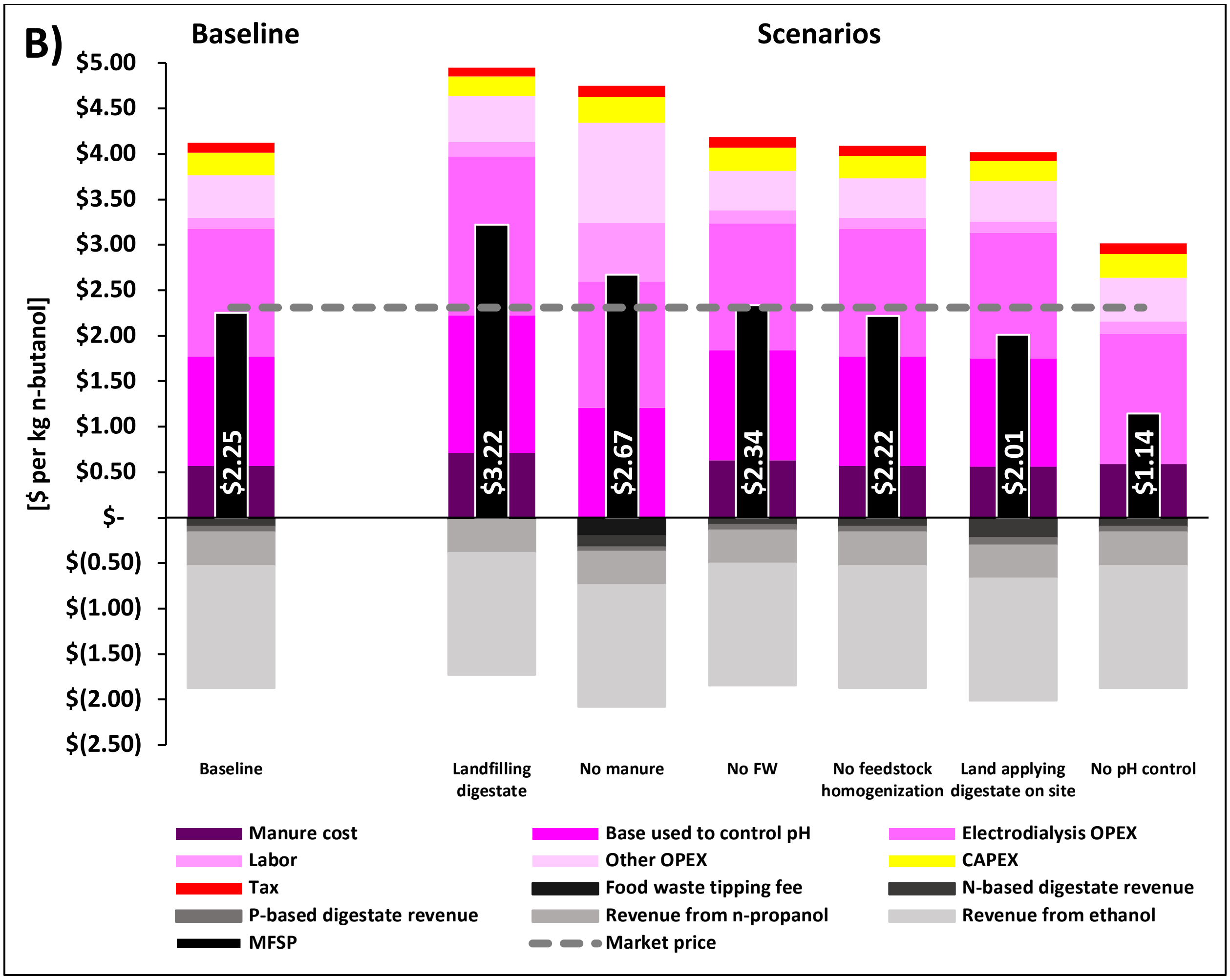


Figure 2: A) Contribution of capital costs, operational costs, tax, and co-product sales to MSP under different assumptions. All impacts are expressed in $ per kg of caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and FW. B) Contribution of capital costs, operational cost, tax, and co-product sales to MSP under different assumptions. All impacts are expressed in $ per kg of n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and FW. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, Solid-Liquid Separation (SLS) of digestate and treatment of liquid digestate before land application. The "no use of digestate" scenario assumes the landfilling of digestate. The "no manure" scenario assumes the use of only FW as a feedstock. The "no FW" scenario assumes the use of only manure as a feedstock. The "no feedstock homogenization" scenario assumes a feedstock total solid% at 9.5% and therefore the absence of feedstock homogenization with water. The "no pH control" scenario assumes the absence of pH control for AD. The "land applying digestate on site" scenario assumes land application of digestate on site with no SLS of digestate and no liquid digestate treatment. (FW: Food Waste; CAPEX: Capital expenditures; OPEX: Operational expenditures; MSP: Minimum Selling Price)

3.1.1.3. Comparing scenarios

Although some similarities between the pathways were discussed previously, there are also differences. For instance, the ethanol procurement cost does not affect the OPEX of the bioconversion pathway because it is not the electron donor in bioconversion (see Figure 1). Instead, the electron donor is hydrogen, and its demand is minimal ($1.62*10^3$ MT·year^{-1}) compared to the high ethanol demand ($102*10^3$ MT·year^{-1}) in the chain elongation pathway. Although the high ethanol demand in the chain elongation pathway results in 53.6% higher CAPEX and 103.3% OPEX compared to the bioconversion pathway, the total carbon conversion efficiency and product yield are higher which offsets the high costs.

Furthermore, base procurement cost on a mass basis is lower in the chain elongation pathway ($0.16 per kg caproic acid) by a factor of 7.5 compared to the bioconversion base cost ($1.21 per kg n-butanol). Similar trends are also observed in Figure 2 for other OPEX because the caproic acid production is higher by a factor of 7.5 compared to the n-butanol production. The higher carbon conversion efficiency and product yield in chain elongation are attributed to the additional carbon provided by ethanol. Additionally, when the two pathways are compared directly on an energy basis, the MSP of caproic acid (0.03 \$·MJ^{-1}) is lower than the MSP of n-butanol (0.06 \$·MJ^{-1}). The baseline MSPs of producing caproic acid is 53.4% lower than the U.S. market price for caproic acid ($2.25 per kg caproic acid) [99]. The MSP of n-butanol generated from wet wastes is only 2.4% lower than the 10-year average US market price of n-butanol ($2.31 per kg n-butanol) [75], [100], as illustrated in Figure 2B. Based on this, the MSP of caproic acid is considerably lower than its market price whereas the n-butanol MSP is close to its market price. Thus, economically, the chain elongation pathway is considered favorable to upgrade VFAs produced from AD due to its higher carbon conversion efficiency, lower OPEX on a mass basis, and its higher potential for economic viability and market competitiveness.

3.1.2. Sensitivity analysis

The baseline MSPs for both pathways are lower than the products' market prices. However, identifying the high impact variables on the MSPs can still aid in further improvements from research and development. Accordingly, a sensitivity analysis was performed on the MSPs to verify model performance and inform the Monte Carlo analysis. The top ten most sensitive modeling parameters obtained from the sensitivity analysis on MSPs of both pathways are illustrated in Figure 3.

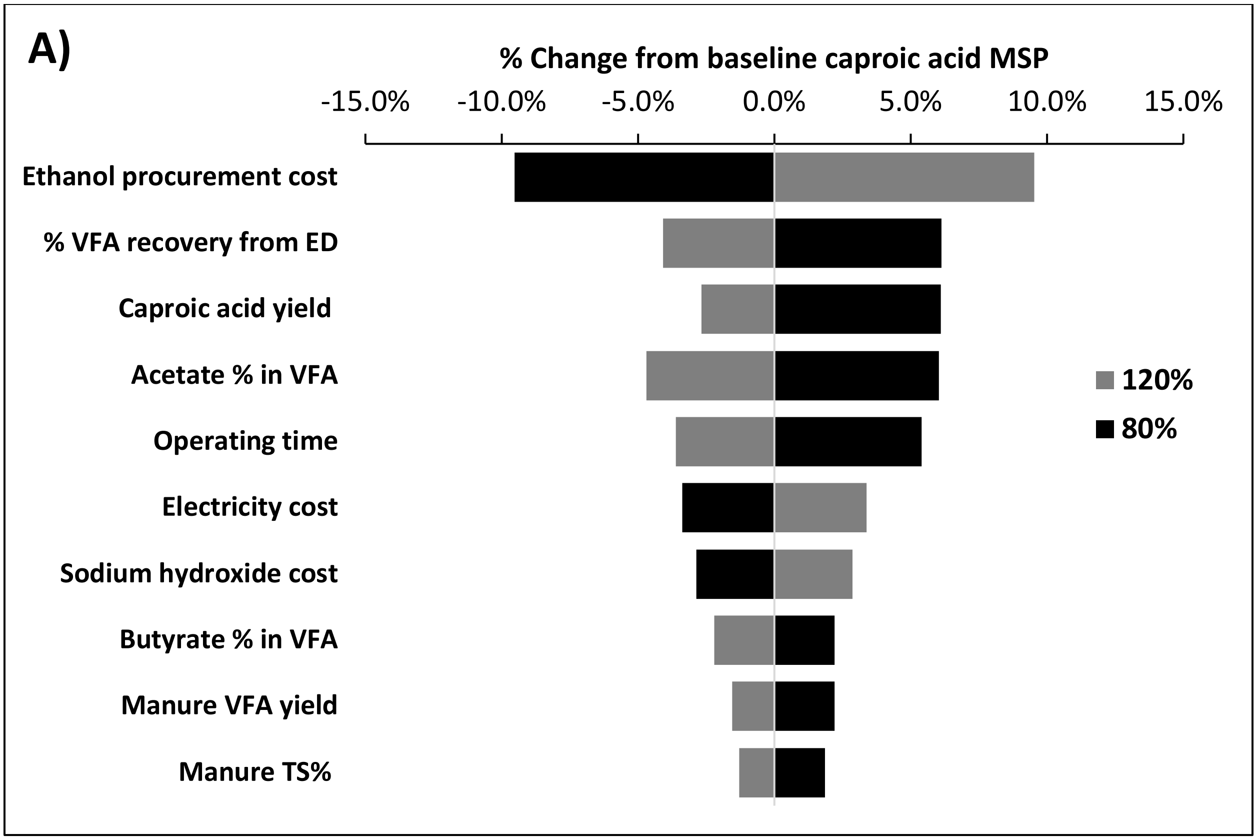
Similarities exist between the sensitivity analysis results of the two pathways, including the high impact of operating time, percent VFA recovery from AD, electricity cost, NaOH cost, manure VFA yield and manure TS%. Operating time is one the most sensitive parameters in both pathways as it is directly correlated to the yields of the system as the total production of VFAs which is the precursor for the main products is impacted. Similarly, percent VFA recovery from AD, manure VFA yield and manure TS% have an impact on the total VFA production of the system. The model responds as expected in terms of change. An increase in yield positively impacts the MSP whereas a decrease negatively impacts the MSP. Conversely to the variables affecting yield, electricity cost and NaOH cost are sensitive variables that negatively impact MSP when increased. They respectively impact the operational costs of ED and the base procurement cost which are large contributors to the OPEX in both pathways as discussed in section 3.1.1. Baseline . The use of the same AD and ED processes in both pathways results in the similarities outlined above.

It is important to note that a decrease in yield shows a larger impact on MSP than an increase in yield as illustrated in Figure 3. Although, it is tempting to assume this is consistent with the economies of scale which are cost advantages obtained due an increase in scale, economies of scale do not have a large impact on the MSPs because CAPEX is a small fraction of the MSPs (see Figure 2). This trend is attributed to upstream OPEX which are not affected by a change in downstream yield. For instance, when caproic acid yield is decreased it does not affect upstream variables such as ethanol cost. The ethanol input behaves as fixed cost and therefore the mass based cost of ethanol increases because there is less product. A 20% decrease in yield causes a larger change than a 20% increase which explains the observed trend (the impact of yield on price on a mass basis is explained in the supplementary materials).

Although the sensitivity analysis results show similarities between the two pathways, they also reveal differences. In the chain elongation pathway, the ethanol procurement cost is the most sensitive input as shown in Figure 3A, this is expected because ethanol procurement cost was the highest contributor to the caproic acid MSP. Although the cost of ethanol is fixed and cannot be used to improve the viability of the system, based on the sensitivity analysis the ethanol demand in the chain elongation pathway is a critical research area. As shown in Figure 1 only acetate and butyrate were used to produce caproic acid in this pathway. Accordingly, the butyrate percent and acetate percent in VFA are in the top 10 most sensitive variables for caproic acid MSP. The higher the production of these VFAs the higher the caproic acid yield. Similarly, the caproic acid yield from acetate, butyrate and ethanol fed to the chain elongation reactor is a highly sensitive input in this pathway because it is directly correlated to the end yield of the system.

Specific to the bioconversion pathway, butyrate percent in VFAs and n-butanol yield impact the n-butanol production in the bioconversion reactor and therefore appear in the top 5 most sensitive input variables (Figure 3B). The ethanol in this pathway is a co-product used to generate revenue and highly offsets the total production cost of n-butanol. Therefore the ethanol price is also a high impact variable in the bioconversion pathway but conversely to the chain elongation pathway it positively impacts the MSP of n-butanol when increased. Another large contributor to the MSP of n-butanol is pH control using NaOH. The higher the production of hydrogen in AD the higher the demand for NaOH to control pH. Naturally, the molar ratio of hydrogen to VFA production in AD is a high impact variable and negatively impacts the MSP of n-butanol when increased.

Using these results, the system's inputs may be optimized to generate competitive market prices for the biochemicals produced from wet wastes. Optimistic scenarios in which the 5 most sensitive inputs are adjusted by ±20% to reduce MSP were investigated and are included in the supplementary data.


A)
% Change from baseline caproic acid MSP
-15.0%
-10.0%
-5.0%
0.0%
5.0%
10.0%
15.0%
Ethanol procurement cost
% VFA recovery from ED
Caproic acid yield
Acetate % in VFA
Operating time
Electricity cost
Sodium hydroxide cost
Butyrate % in VFA
Manure VFA yield
Manure TS%
120%
80%

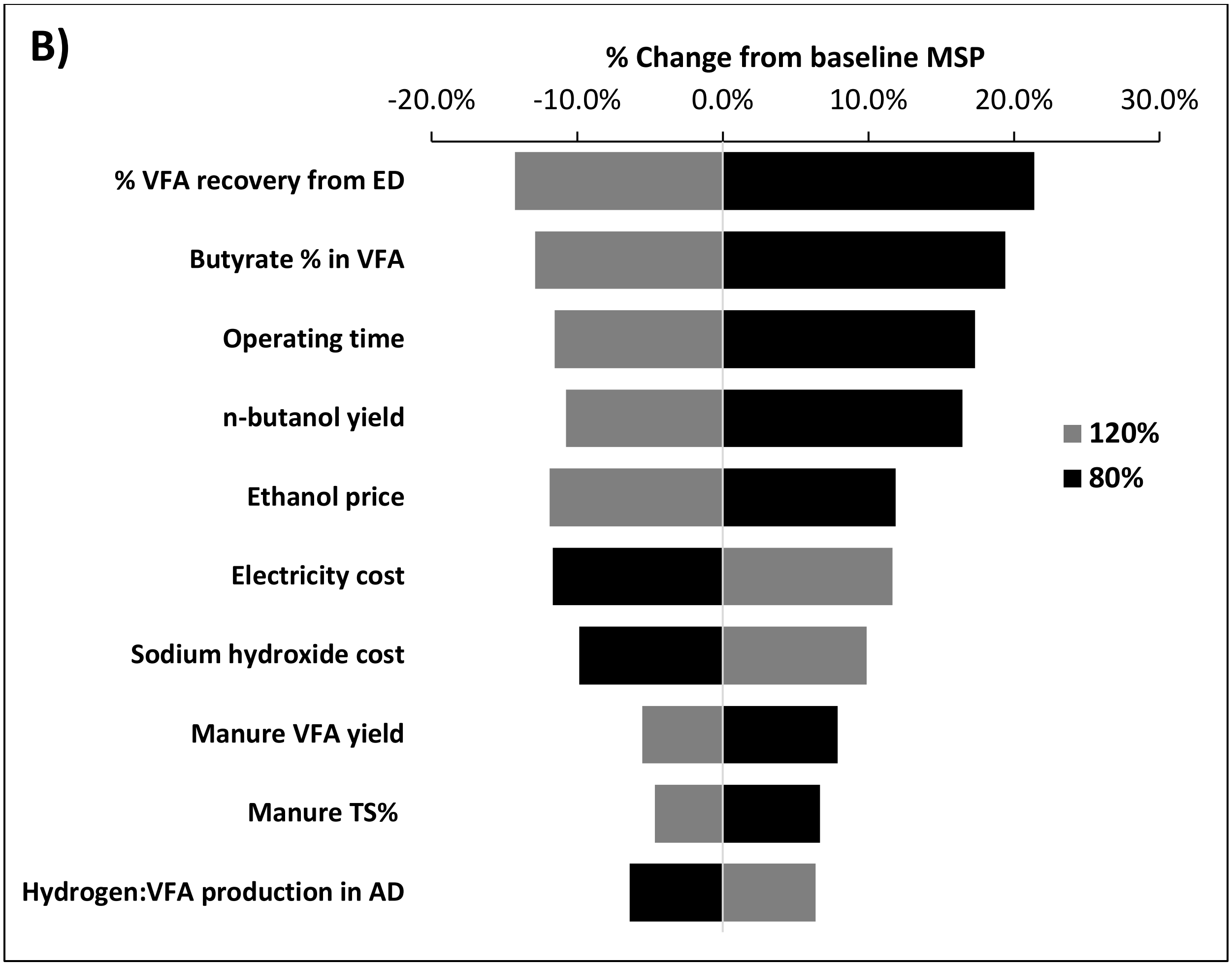


Figure 3: A) The ten most sensitive modeling parameters, with respect to MSP for a baseline scenario of caproic acid production from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) The ten most sensitive modeling parameter, with respect to MSP for a baseline scenario of n-butanol production from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The black bars indicate the corresponding delta in MSP ($ per kg biochemical) for a 20% decrease in the input variable. The grey bars indicate the corresponding delta in MSP ($ per kg biochemical) for a 20% increase in the input variable. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (MSP: Minimum Selling Price; ED: Electro-Dialysis; VFA: Volatile Fatty Acid; TS: Total Solids)

3.1.3. Scenario analysis

Sensitivity analysis does not account for whole process-level changes and is limited to model functionality. Scenarios investigating the impact of sensitive input assumptions were completed and the results are presented in Figure 2. Accordingly, "no manure" and "no FW" scenarios were used to understand the impact of feedstock on the MSPs of caproic acid and n-butanol. The absence of manure results in higher MSPs for both caproic acid (1.09 $\$\cdot kg^{-1}$) and n-butanol (2.67 $\$\cdot kg^{-1}$) as manure increases the scale of the system considerably which leads to a lower MSP based on total availability. The higher VFA yield of FW compared to manure (see Table 1) makes the use of a small amount of FW decrease the MSPs slightly. Based on the results illustrated in Figure 2, co-digestion of manure and FW is favorable and reduces the MSP. Sodium hydroxide and water are used to control pH and homogenize feedstock, respectively. A recent research study demonstrated the electrolytic extraction of VFAs produces OH^- providing an alternative to controlling pH [101]. Moreover, many digesters were recorded to operate at a higher TS% than the baseline (9.5 TS %) used in this this model [45]. Accordingly, "no feedstock homogenization" and "no pH control" scenarios were used to determine the impact of these sub-processes on the MSPs. The results show the feedstock homogenization step has a minimal impact on the MSP whereas the absence of pH control reduced the MSPs by 14.4% for caproic acid and 49.4% for n-butanol. This is consistent with the large contribution of base procurement cost to OPEX in both the chain elongation (15.8%) and bioconversion (32.1%) pathways.

Although, digestate based fertilizers do not provide large co-product credits, "landfilling digestate" and "land applying digestate on site" scenarios were investigated to better capture the impact of digestate handling on caproic acid and n-butanol MSPs. Economic results illustrated in Figure 2, show the landfilling of digestate has a large influence on the production cost of both caproic acid and n-butanol. When digestate is landfilled the MSP increases by 12.6% for caproic acid and 43.0% for n-butanol. This large impact results mainly from the cost associated with landfilling digestate ($\$20\cdot ton^{-1}$) as animal manure [102] but also from the absence of revenue from digestate based fertilizers. Therefore it is necessary to avoid landfilling digestate and use it as a potential fertilizer. If the local farmland is poor in nutrients digestate can be land applied on site reducing the MSPs for caproic acid and n-butanol by 3.0% and 10.8%, respectively. The abscense of digestate treatment steps in this scenario results in more N and P available for crop uptake which increases co-product sales of digestate based fertilizers as illustrated in Figure 2. These results demonstrate the important role the digestate handling and treatment plays in reducing the MSP.

Although all scenarios showed similar trends for both pathways, all scenarios for caproic acid remained under market price whereas for n-butanol some scenarios resulted in MSPs higher than market price. Upgrading VFAs to caproic acid is again favorable due to its higher potential for economic viability and market competitiveness under different scenarios. It is important to note the chain elongation pathway is less sensitive to changes in assumptions because of its higher product yield. Understanding the highly sensitive input variables and the impact of different scenarios on MSPs can help guide future research. Accordingly, it is recommended for both pathways, that future research focus on minimizing costs associated with manure procurement, pH control, the energy demand of ED, and increasing the yields and efficiencies of all processes. Specific to the chain elongation pathway, future research must focus primarily on reducing ethanol demand for caproic acid production. Whereas in the bioconversion pathway future research must focus on diverting the VFA profile to more butyrate production to produce more n-butanol.

3.2. Life Cycle Assessment

The energy and mass balances of the engineering process models of the two pathways were combined with LCI data to investigate the GHG emissions associated with producing caproic acid and n-butanol from AD of manure and FW. The LCA generated GWPs for both pathways, and a sensitivity analysis was conducted to determine critical research areas and inform the Monte Carlo analysis. Solutions to reduce the environmental impacts of the system are discussed.

3.2.1. Baseline global warming potential

The GHG emissions resulting from producing caproic acid and n-butanol from wet wastes are presented in Figure 4A and Figure 4B, respectively. Emissions are expressed in thousand MT CO_2-eq·year^{-1}. The LCA shows both pathways result in net positive GHG emissions. The positive results are mainly attributed to the emissions associated with the electricity demand in ED, digestate storage, base to control pH and CO_2 production in AD. These emissions are consistent in both pathways. The high impact of emissions associated with ED electricity demand and base to control pH corroborate their high impact on the economics of the system discussed in section 3.1. Techno-economic analysis. Digestate storage contributed significantly to emissions in both pathways because it releases methane when it is stored in an open tank. The high methane emissions from digestate storage are consistent with LCA results in Whiting and Azapagic [92]. Although storing digestate has large emissions associated with it, emissions credits associated with digestate fertilizer produced reduce the overall emissions. However, emissions credits associated with generating digestate fertilizers are minimal compared to the credits applied for diverting waste from traditional processing, as observed in Figure 4.

There are similarities between the two pathways as discussed above but there are also differences. Particularly in the chain elongation pathway, the emissions associated with ethanol production highly impact the GWP of caproic acid production. This is in agreement with the high ethanol demand and its impact on the economics of the chain elongation pathway. The LCA generates a GWP of 2.2 kg CO_2–eq per kg of caproic acid. Chen et al. [19] demonstrated that the life cycle GWP of producing 1 kg of caproic acid from the biological acidification of mixed organic waste and chain elongation of acetate was 8.7 kg CO_2–eq. The lower GWP for caproic acid production from manure and FW is attributed to the emissions credits associated with the diversion of waste from traditional processing and generating digestate based fertilizers. When the inputs in this work are harmonized with Chen et al. [19] the results are very similar, 8.1% difference. Caproic acid has many applications and is conventionally produced from food crops like palm and coconut [19]. Chen et al. [19] estimated the GHG emissions of palm oil based caproic acid at 0.23 kg CO_2–eq per kg. The chain elongation pathway emissions are considerably higher than the GHG emissions estimation for caproic acid from palm oil. However, this estimation has many uncertainties, including the extraction efficiency of caproic acid from palm oil, effects of land use change and the unknown impacts of downstream processes, as explained by Chen et al. [19]. Nevertheless, based on this the caproic acid production from wet waste will need substantial improvements to become environmentally favorable.

Specific to the bioconversion pathway, the displacement credits are also dominated by the upstream credits of utilizing manure and FW. Based on the LCA on the baseline bioconversion pathway and when co-products are credited by energy allocation the well to gate GWP of n-butanol is 24.0 g CO_2–eq·$MJ_{n\text{-butanol}}^{-1}$. Butanol is a high value product and could be used as a chemical feedstock and would likely replace fossil butanol [103]. The GHG emissions of fossil butanol were retrieved from the Ecoinvent database for butanol produced by hydroformylation of propylene and calculated according to the TRACI methodology to be 88.5 g CO_2–eq·$MJ_{n\text{-butanol}}^{-1}$. Therefore, the bioconversion pathway GWP of n-butanol achieves a 73.0% reduction in GHG emissions compared to fossil butanol. It is important to note that this only comprises the production of n-butanol, not the embodied carbon within the fossil butanol. If the carbon embodied in the butanol is released to the atmosphere at the end-of-life of the chemical, this saving would be even higher, because the embodied carbon in fossil butanol is fossil carbon, whereas biogenic carbon does not contribute to the total global warming based on the carbon accounting methods in this study. Additionally, the conventional production of biobutanol is acetone-butanol-ethanol (ABE) fermentation and the well-to-wheels GHG emissions of corn-based butanol are 63.5 g CO_2–eq·$MJ_{n\text{-}butanol}^{-1}$[104]. The well-to-wheels GWP for the bioconversion pathway was estimated to be 25.2 g CO_2–eq·$MJ_{n\text{-}butanol}^{-1}$ by adding emissions associated with transportation/distribution of butanol [104]. Therefore, the bioconversion of VFAs produced from AD also presents an environmental advantage compared to the conventional biobutanol production.

In recent years, butanol has been regarded as a potential biofuel substitute for gasoline [104]. However, for an advanced fuel to qualify as renewable fuel under the renewable fuel standard (RFS) program it must meet a 50% lifecycle GHG reduction threshold compared to the 2005 petroleum baseline [105]. The GHG emissions estimate reported for the bioconversion pathway induce 71.0% potential savings of GHG emissions compared to the gasoline well-to-wheels baseline (87.1 g CO_2–eq·MJ^{-1}) [106]. Therefore, it can be concluded that the production of n-butanol from VFAs will be a highly viable pathway environmentally.

The emissions associated with the pathways are compared to conventional AD to better capture its environmental viability. Manure biomethane is reported to range from -44 to 72 g CO_2–eq·MJ^{-1} depending on upstream methane leakage emissions and credits assumed for displacement of artificial fertilizers by digestate [107]. The GWPs of caproic acid and n-butanol are within this range. Therefore, using the baseline assumptions, diverting AD from low value methane to VFAs and upgrading those does not reduce the environmental viability of AD. A sensitivity analysis is necessary to identify the high impact variables on the GWPs and aid in guiding research into a system optimized for environmental sustainability discussed in section 3.2.3.

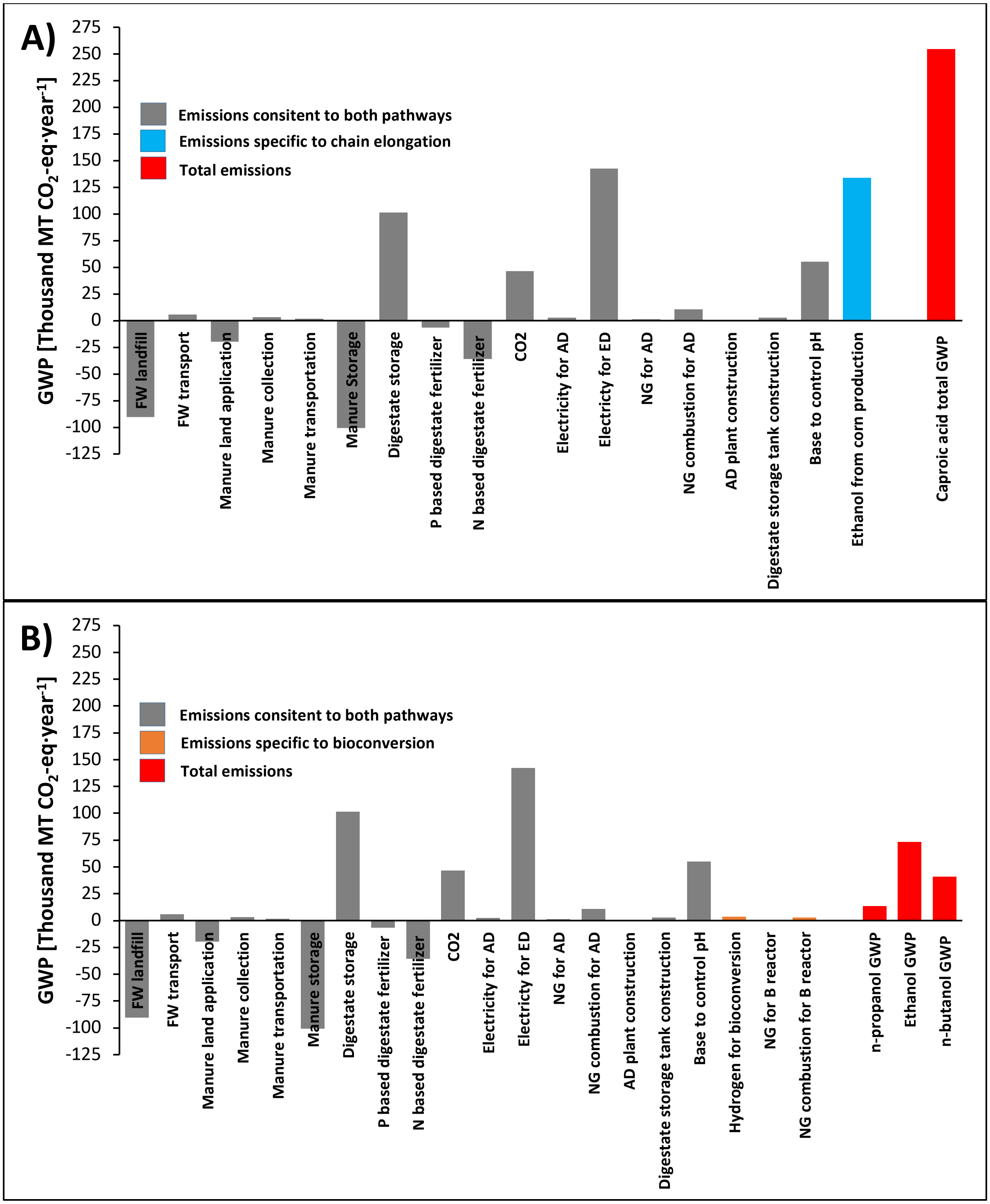


Figure 4: A) Contribution of different life cycle stages to the GWP of caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and FW. B) Contribution of different life cycle stages to the GWP of n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and FW. All impacts are expressed in thousand MT CO_2-eq per year. The results illustrate a baseline scenario that assumes the use of feedstock water homogenization, pH control in AD, ED to

recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: Food Waste; P: Phosphorus; N: Nitrogen; AD: Anaerobic Digester; ED: Electro-Dialysis; NG: Natural Gas; CE: Chain Elongation; B: Bioconversion; GWP: Global Warming Potential)

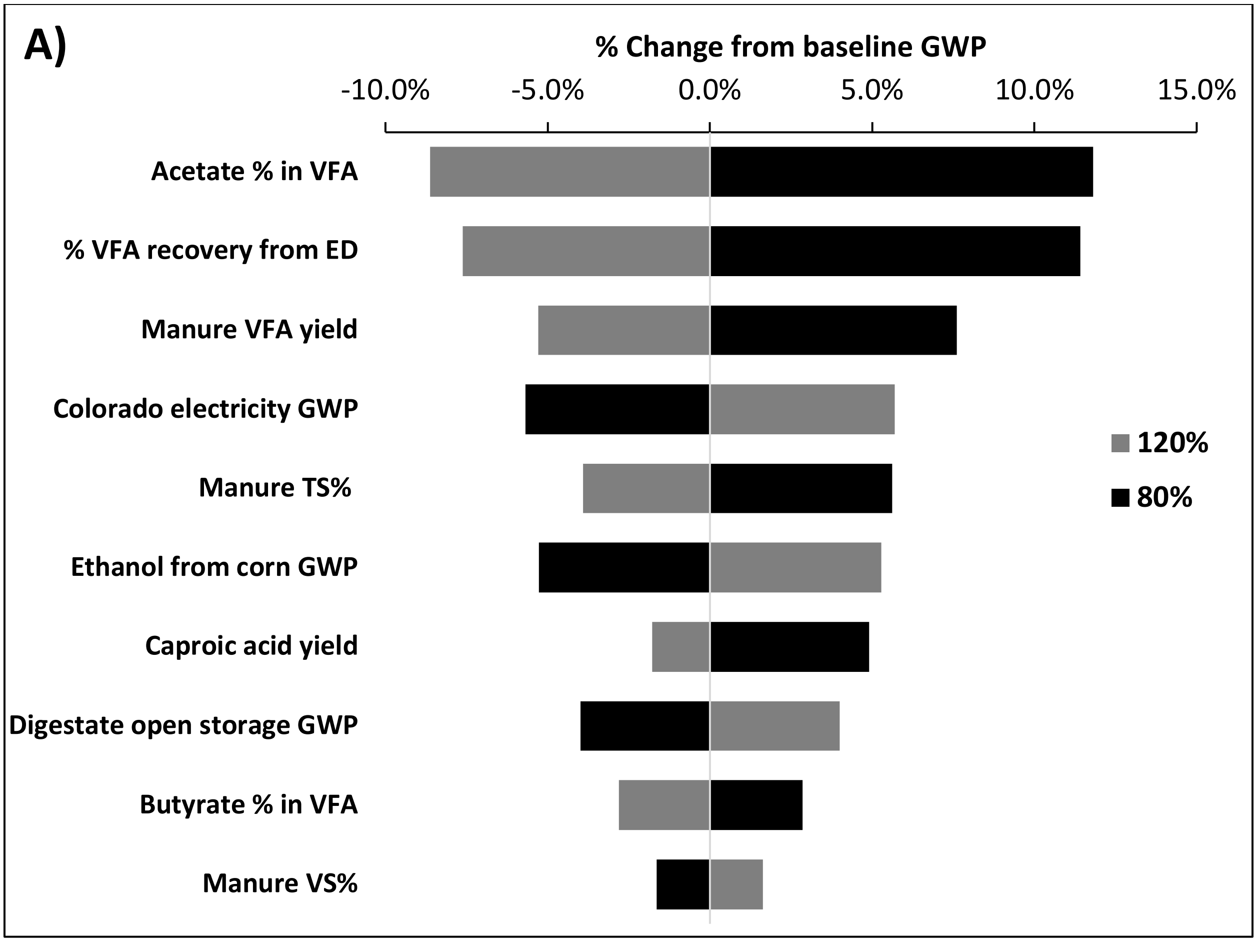
3.2.2. Sensitivity analysis

Similar to the TEA work, a sensitivity analysis was performed on the GWPs to determine the top ten most sensitive variables in both pathways. The results are presented in Figure 5. Many of the highly sensitive variables are similar in both pathways, including the percent VFA recovery from ED, manure VFA yield, manure TS%, electricity GWP and digestate storage GWP. Variables related to the total VFA production affect the total energy output of the system and therefore positively impact the GWP when increased. More specifically, the acetate percent in VFA is the most sensitive input in both pathways because the VFA profile is dominated by acetate. Additionally, digestate storage GWP is a high impact variable because of the high emissions associated with storing digestate in an open tank. The GWP of electricity is also a high impact variable because the high electricity demand of ED.

Specific to the chain elongation pathway, the sensitivity analysis presented in Figure 5A identifies ethanol production GWP as a highly sensitive variable similar to the economic results. Butyrate percent in VFAs and the caproic acid yield in chain elongation are shown to be high impact variables justifiably as they impact the final caproic acid yield. Finally, the high sensitivity of manure VS% is justified by its direct correlation to CO_2 production in AD which is a high contributor to emissions. Previous research studies determined that CO_2 may be reduced by a homoacetogenesis which produces acetate [5].

In the bioconversion pathway, percent acetate in VFAs, percent propionate in VFAs and ethanol yield from acetate are highly sensitive input variables because they impact the GHG allocation and total energy output of the system. When these variables increase, the GHG emissions allocated to n-butanol decrease which decreases the GWP of n-butanol (see Figure 5B) but increases the GWP per mega joule of total biofuel produced. Conversely, increasing percent butyrate in VFAs and n-butanol yield from butyrate leads to an increase in the energy allocated to n-butanol which increases the GWP per mega joule of total biofuel produced.

Future research in both pathways must focus on improving yields, reducing electricity demand of ED and reducing emissions from digestate storage. Specific to chain elongation future research should focus on reducing ethanol demand, finding an alternative to corn-based ethanol and increasing acetate production using homoacetogenesis of CO_2. To achieve a lower GWP for n-butanol future research may target a VFA profile dominated by acetate and propionate.


A)
% Change from baseline GWP
-10.0%
-5.0%
0.0%
5.0%
10.0%
15.0%
Acetate % in VFA
% VFA recovery from ED
Manure VFA yield
Colorado electricity GWP
Manure TS%
Ethanol from corn GWP
Caproic acid yield
Digestate open storage GWP
Butyrate % in VFA
Manure VS%
120%
80%

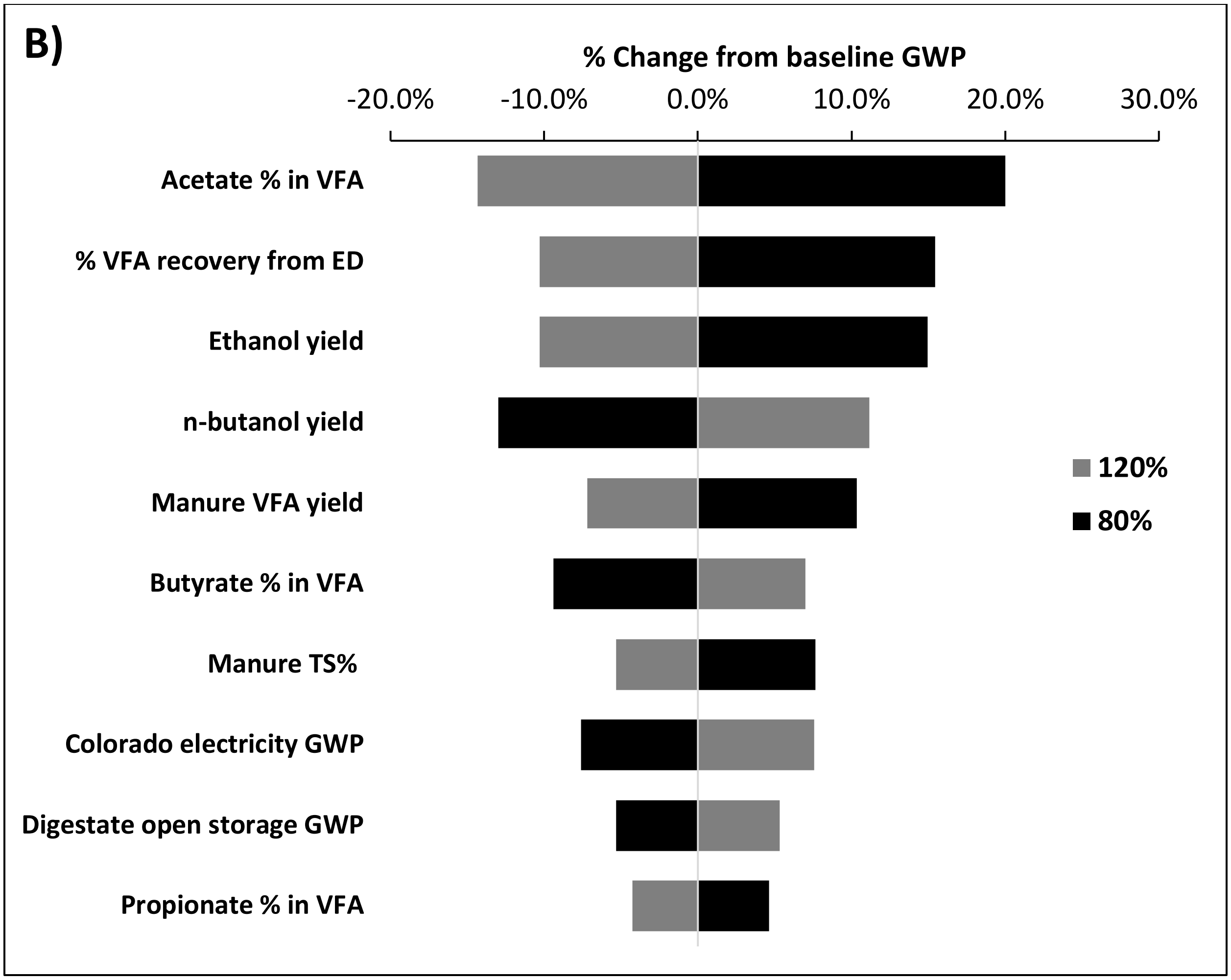


Figure 5: A) The ten most sensitive modeling parameters, with respect to GWP for a baseline scenario of caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) The ten most sensitive modeling parameter, with respect to GWP for a baseline scenario of n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The black bars indicate the corresponding delta in GWP (g CO_2-eq·$MJ_{biochemical}^{-1}$) for a 20% decrease in the input variable. The grey bars indicate the corresponding delta in GWP (g CO_2-eq·$MJ_{biochemical}^{-1}$) for a 20% increase in the input variable. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. Credits are ignored in the Monte Carlo analysis. (ED: Electro-Dialysis; VFA: Volatile Fatty Acid; FW: Food Waste; AD: Anaerobic Digester; GWP: Global Warming Potential; NG: Natural Gas; TS: Total solids; VS: Volatile solids)

3.2.3. Scenario analysis

High impact variables determined from LCA and sensitivity analysis are used to simulate an ideal scenario that reduces the emissions associated the chain elongation and bioconversion pathways. First, the GHG emissions of electricity are based on the 2021 Colorado electricity grid mix (484 g CO2-eq·kWh^{-1}). To reduce the GHG emissions associated with electricity in both pathways, the system could assume a cleaner grid using the 2050 Colorado electricity grid mix (218 g CO2-eq·kWh^{-1}) [108]. Furthermore, the baseline conservative scenario assumed the use of an open tank to store the digestate, the storage emissions can be reduced considerably by using a closed tank to store the digestate. The gas emissions from digestate in a closed tank (0.03 kg CO_2-eq·kg digestate^{-1}) are 77% lower than gas emissions from an open tank [92]. Although a closed tank has higher capital costs, this change would minimally impact the economics of the system because of the low impact of CAPEX on the MSPs.

Specific to the chain elongation pathway, corn-based ethanol (1,318 g CO2-eq·kg ethanol^{-1}) has a higher GWP than sugar cane-based ethanol (663 g CO2-eq·kg ethanol^{-1}) which is already available at a large production scale [19], [87]. The GWP for chain elongation is dramatically reduced to 0.23 kg CO_2–eq per kg caproic acid if a cleaner electricity grid mix, a closed tank to store digestate and sugar cane-based ethanol are used.

In the bioconversion pathway, using a cleaner electricity grid mix and storing digestate in a closed tank result in net negative GHG emissions (-6.3 g CO_2–eq·$MJ_{n\text{-butanol}}^{-1}$). This GWP for n-butanol induces 106.2% potential savings of GHG emissions compared to the gasoline well-to-wheels baseline [106]. The alternative assumptions improve the environmental sustainability of both pathways and help achieve negative carbon intensity in the bioconversion pathway. The negative result is attributed to the emissions credits associated with the diversion of waste from traditional processing. Conversely to the economic analysis, in all the scenarios the GWP of n-butanol is lower than caproic acid, illustrating the higher environmental viability of bioconversion.

3.3. Monte Carlo analysis

The novelty of the technologies evaluated in this study includes inherent uncertainty due to a lack of large scale real-world data. Monte Carlo uncertainty analysis is used to understand the certainty of model results. Accordingly, the top five most sensitive parameters obtained from the sensitivity analysis on MSP and GWP were assigned distributions described in Table 3 and 10,000 iterations were conducted for each of the pathways' MSP and GWP.

3.3.1. Minimum selling price

The Monte Carlo results for caproic acid MSP show a standard deviation of \$0.13 per kg caproic acid from an average of \$1.06 per kg caproic acid. The median presents a 2.45% difference from the baseline MSP for caproic acid. The minimum (min) and maximum (max) MSPs within the 90% confidence interval are \$0.85 per kg caproic acid and \$1.27 per kg caproic acid, respectively. The bimodal probability distribution for MSP of caproic acid presented in Figure 6A is consistent with the bimodal distribution of ethanol price (see supplementary materials), the highest impact variable in chain elongation. The results demonstrate that even if the high impact parameters are chosen randomly within their assigned distributions, the model yields a MSP that is always lower than the market price for caproic acid (Figure 6A). This shows the high probability of economic success in the chain elongation pathway.

The Monte Carlo analysis performed on the MSP of n-butanol generated a 90% confidence interval between 1.44 $\$\cdot kg^{-1}$ and 3.10 $\$\cdot kg^{-1}$. The median and average show an error of 0.05% and 0.73% from the baseline value with a standard deviation of \$0.51 per kg n-butanol. The Monte Carlo analysis on MSP of n-butanol shows a lower probability of economic success compared to caproic acid because market price of n-butanol falls within the 90% confidence interval. Therefore, in the bioconversion pathway the high impact inputs must be optimized through research and development to achieve market competitiveness. The results demonstrate a higher certainty associated with the baseline MSP of caproic acid because the standard deviation is higher for the n-butanol MSP. However, it is important to note that the caproic acid yield, a high impact variable in chain elongation, was not assigned a distribution (see Table 3) due to lack of supporting data. Future experimental data will generate a distribution for the caproic acid yield which will help refine the results.

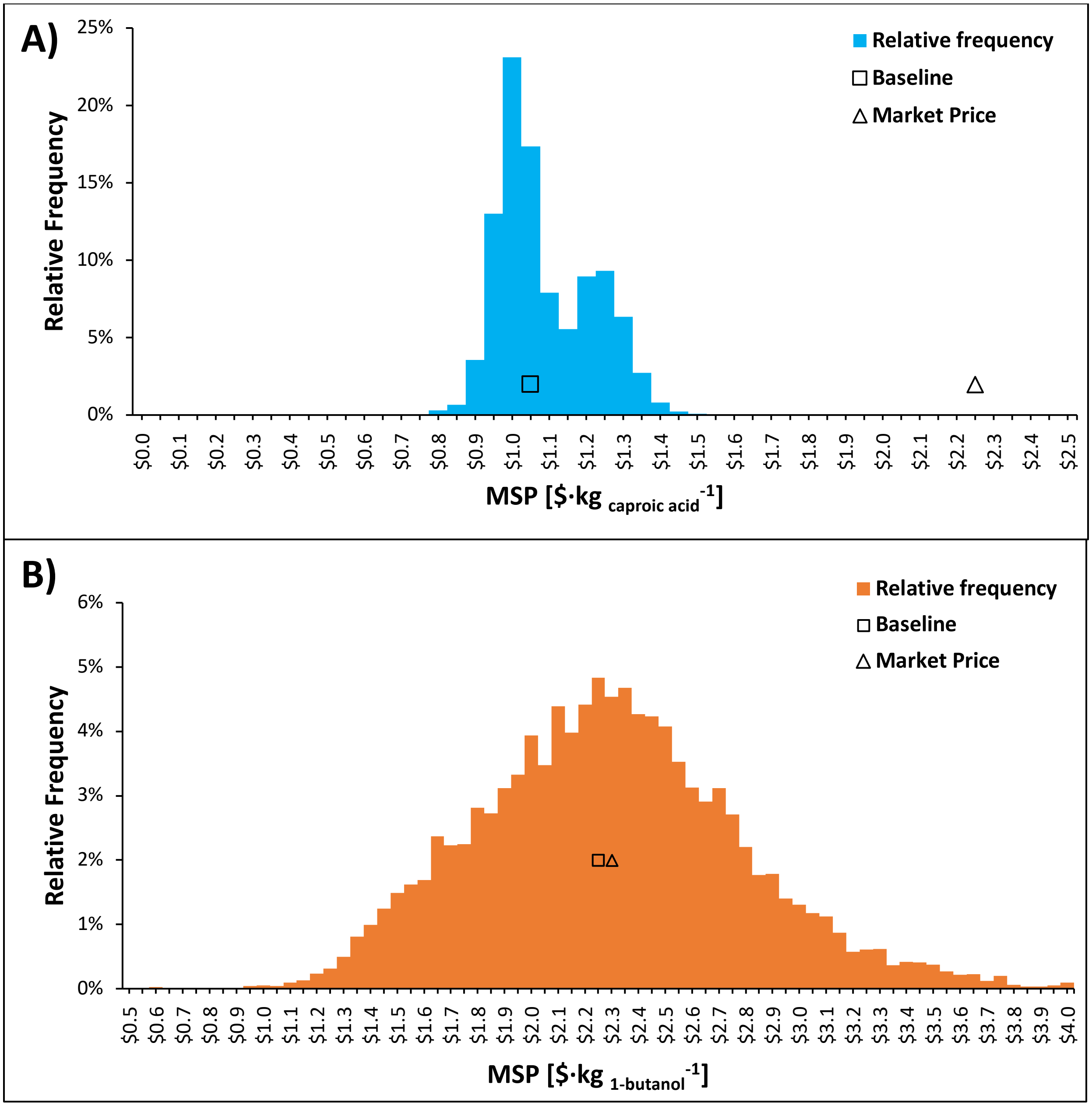


Figure 6: A) Monte Carlo analysis results for the caproic acid MSP probability distribution. The MSP is expressed in $\$\cdot$kg caproic acid^{-1} produced from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) Monte Carlo analysis results for n-butanol MSP. The MSP is expressed in $\$\cdot$kg n-butanol^{-1}produced from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The grey bars indicate the corresponding probability density of that given value occurring out of the 10,000 iterations performed in each analysis. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (MSP: Minimum Selling Price; SLS: Solid-Liquid Separation)

3.3.2 Global warming potential

The Monte Carlo analysis executed on the GWP without credits of caproic acid is presented in Figure 7A. The analysis shows a 147.4 g CO_2-eq·$MJ_{caproic\ acid}^{-1}$ average with a standard deviation of 11.5 g CO_2-eq·$MJ_{caproic\ acid}^{-1}$. The median value shows a 1.4% error from the baseline estimate (143.9 g CO_2-eq·$MJ_{caproic\ acid}^{-1}$). Furthermore, the Monte Carlo analysis yields a left leaning lognormal distribution with a 90% confidence interval from 128.5 to 166.3 g CO_2-eq·$MJ_{caproic\ acid}^{-1}$. For the GWP of n-butanol, the Monte Carlo analysis presented in Figure 7B shows a 90% confidence interval from 58.2 to 96.4 g CO_2-eq·$MJ_{n\text{-}butanol}^{-1}$, respectively. The standard deviation for the analysis is 11.87 g CO_2-eq·$MJ_{n\text{-}butanol}^{-1}$. The average and median show a 5.81% and 4.30% error from the baseline value (71.4 g CO_2-eq·$MJ_{n\text{-}butanol}^{-1}$).

The higher standard deviation of n-butanol GWP demonstrates the lower certainty associated with the n-butanol GWP compared to the caproic acid GWP. The higher standard deviations in both the bioconversion MSP and GWP compared to the chain elongation corroborates the higher sensitivity observed in the bioconversion pathway that is associated to the production of less n-butanol compared to caproic acid.

The Monte Carlo results demonstrate the certainty of economic success for chain elongation and the need for more research and development to achieve market competitiveness for bioconversion. Additionally, Monte Carlo demonstrates the higher certainty associated with the MSP and GWP of caproic acid which corroborates the lower sensitivity to change observed for the chain elongation pathway which was attributed to the higher product yield compared to the bioconversion pathway. Future research should therefore focus on increasing the yield of n-butanol to improve the viability of the bioconversion pathway.

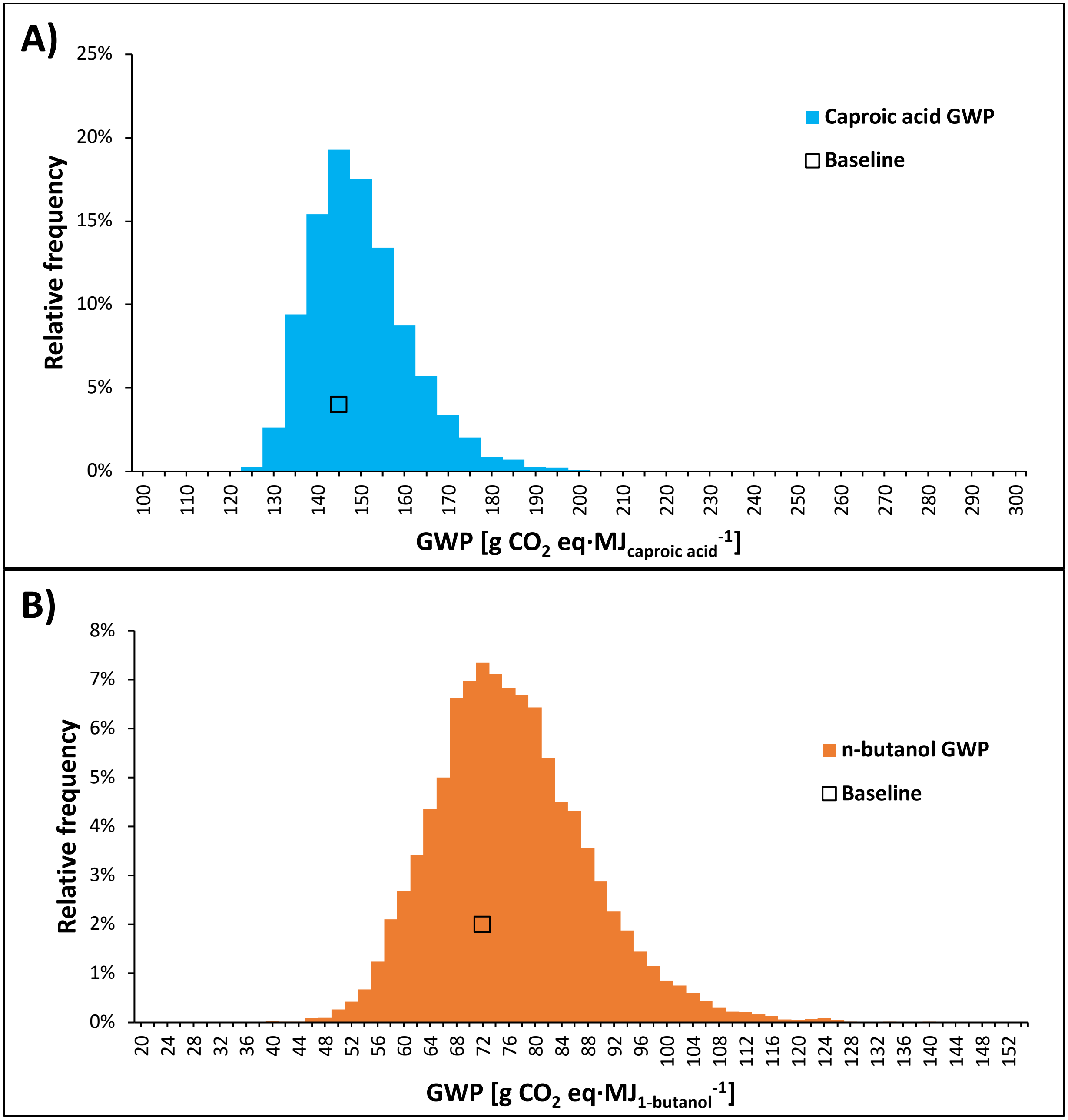


Figure 7: A) Monte Carlo analysis results for the caproic acid GWP. The GWP is expressed in g CO_2-eq·$MJ_{caproic\ acid}^{-1}$ for caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) Monte Carlo analysis results for n-butanol GWP. The GWP is expressed in g CO_2-eq·$MJ_{n\text{-}butanol}^{-1}$ for n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The grey bars indicate the corresponding probability density of that given value occurring out of the 10,000 iterations performed in each analysis. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. Credits are ignored in the Monte Carlo analysis. (GWP: Global Warming Potential; SLS: Solid-Liquid Separation)

4. CONCLUSIONS

This study evaluates the economic and environmental viability of diverting AD from low value methane to VFAs that can be upgraded to economically attractive biochemicals such as caproic acid and n-butanol. Chain elongation is used to produce caproic acid and bioconversion is used to produce n-butanol. The TEA results in economically favorable MSPs of \$1.05 per kg caproic acid^{-1} and \$2.25 per kg n-butanol for the two different pathways evaluated. Although, the operational costs associated with energy demand of ED, base procurement and manure procurement were large contributors to the MSPs in both pathways, the ethanol procurement cost dominated the caproic MSP. Using displacement credits and accounting for emissions associated with each process, the baseline LCA yields an environmentally unfavorable GWP of 72.1 g CO_2-eq$\cdot$$MJ_{caproic\ acid}^{-1}$ for the chain elongation pathway. The LCA results show GHG emissions of 24.0 g CO_2-eq$\cdot$$MJ_{n\text{-}butanol}^{-1}$ for the bioconversion pathway which qualifies it as a renewable fuel under the RFS program. Sensitivity and scenarios analyses were used to identify critical research areas to improve the sustainability of the pathways. The digestate handling and treatment, energy demand of ED, pH control in AD and improving yield efficiencies were identified as important research areas in both pathways to improve the performance of the technology both economically and environmentally. Specific to the chain elongation pathway, future research must primarily focus on finding an alternative to ethanol as an electron donor or reduce its demand. Using high impact variables determined from the sensitivity analysis results, emissions are dramatically decreased for caproic acid and net negative emissions are achieved for the n-butanol production. The results from this study demonstrate that producing biochemicals from wet wastes is economically and environmentally sustainable. If the technology can be successfully integrated in the wet waste treatment industry to reduce the environmental impacts of food waste and manure, there is a huge potential to transform AD to an economically attractive technology.

5. RECOMMENDED FUTURE RESEARCH

- Gather additional experimental data to simulate biochemical production from wet waste to ensure higher fidelity modeling results.
- Develop models to further understand the electrons' demand in anaerobic digestion and the impact of electricity on anaerobic digestion.
- Develop dynamic models to further understand the impact of feedstock, and anaerobic digester temperature and pH on VFA profile.
- Develop a model for electrolytic extraction of VFAs inside the anaerobic digester to further understand base demand to control pH.
- Model anaerobic digester, chain elongation and bioconversion in Aspen plus and include recycle streams to ensure higher fidelity modeling results.
- Gather additional cost data and develop a model to simulate the use of alternative bases.
- Gather additional cost data and develop a model to simulate the use of waste water for feedstock homogenization and the use of waste ethanol for chain elongation and understand the impact of the system's efficiency, and economic and environmental viability.
- Expand system boundary to include transportation and field application of digestate, and distributions and use of caproic acid and n-butanol to further understand economic and environmental impacts of biochemical production from wet waste using enhanced anaerobic digestion.

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APPENDIX A. SUPPLEMENTARY MATERIALS

Table A. 1. The investment cost of sub-processes for caproic acid and n-butanol production from VFAs produced from anaerobic digestion of wet wastes. (CAPEX: capital expenditure; CSTR: continuous stirred tank reactor; VFA: volatile fatty acid)

Equipment name	Original equipment cost	Base year	Scaling variable	Units	Number of units in System	Scaling factor	New variable	Units	Uninstalled cost	Installation Factor	Installed cost	Installed cost in 2018
Anaerobic digester	$566,000	2010	4,210	m^3	1	0.6	50,448	m^3	$2,511,621	1	$2,511,621	$2,757,115
Anaerobic digester	$6,450,000	2012	102,206	m^3 per unit	1	0.6	50,448	m^3 per unit	$4,222,606	1	$4,222,606	$4,356,233
Anaerobic digester average CAPEX [c, d]	-	-	-	-	-	0.6	-	-	-	1	-	$3,556,674
Electrodialysis [c, d]	-	2002	-	-	-	0.6	-	-	-	2	$16,850,816	$25,754,503
Decanter Centrifuge [c, d]	$275,000	2015	80	$m^3 \cdot hr^{-1}$	1	0.6	96	$m^3 \cdot hr^{-1}$	$306,554	1	$306,554	$332,046
Stripping Column [c, d]	$4,000,000	2009	24,123	kmol air$\cdot hr^{-1}$	1	0.6	7,367	kmol air$\cdot hr^{-1}$	$1,963,276	1	$1,963,276	$2,278,775
Absorbing Column [c, d]	$4,810,000	2009	24,123	kmol air$\cdot hr^{-1}$	1	0.6	7,367	kmol air$\cdot hr^{-1}$	$2,360,839	1	$2,360,839	$2,740,227
Nitrifying Reactor [c, d]	$566,000	2010	4210	m^3	1	0.6	2,609	m^3	$424,705	1	$424,705	$466,217
Chain elongation CSTR 1 [c]	$55,000	2016	29,400	L	358	0.6	29,329	L	$19,661,431	1	$19,661,431	$21,889,993
Chain elongation CSTR 2 [c]	$55,000	2016	29,400	L	181	0.6	29,308	L	$9,936,330	1	$9,936,330	$11,062,582
Chain elongation CSTR 3 [c]	$55,000	2016	29,400	L	65	0.6	29,110	L	$3,553,810	1	$3,553,810	$3,956,623
Chain elongation CSTR 4 [c]	$55,000	2016	29,400	L	23	0.6	29,344	L	$1,263,555	1	$1,263,555	$1,406,775
Bioconversion CSTR 1 [d]	$55,000	2016	29,400	L	137	0.6	29,212	L	$7,506,081	1	$7,506,081	$8,356,872
Bioconversion CSTR 2 [d]	$55,000	2016	29,400	L	55	0.6	29,228	L	$3,014,351	1	$3,014,351	$3,356,018
Bioconversion CSTR 3 [d]	$55,000	2016	29,400	L	16	0.6	29,099	L	$874,591	1	$874,591	$973,724

[c] CAPEX specific to the chain elongation pathway.
[d] CAPEX specific to the bioconversion pathway.

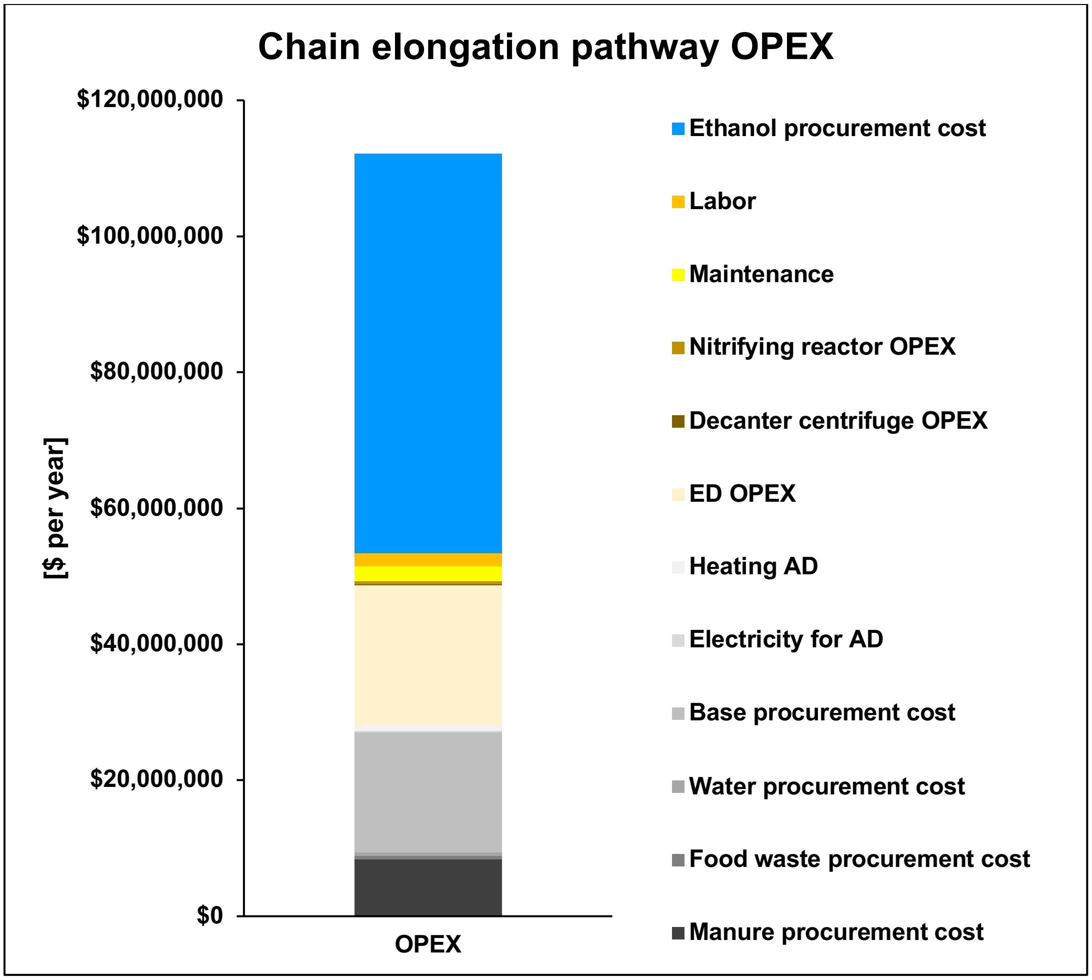


Figure A. 1. OPEX distribution for baseline caproic acid production by chain elongation of VFAs produced from AD of manure and FW. All OPEXs are expressed in $ per year. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: food waste; OPEX: operational expenditures; ED: electrodialysis; AD: anaerobic digestion; VFA: volatile fatty acid)

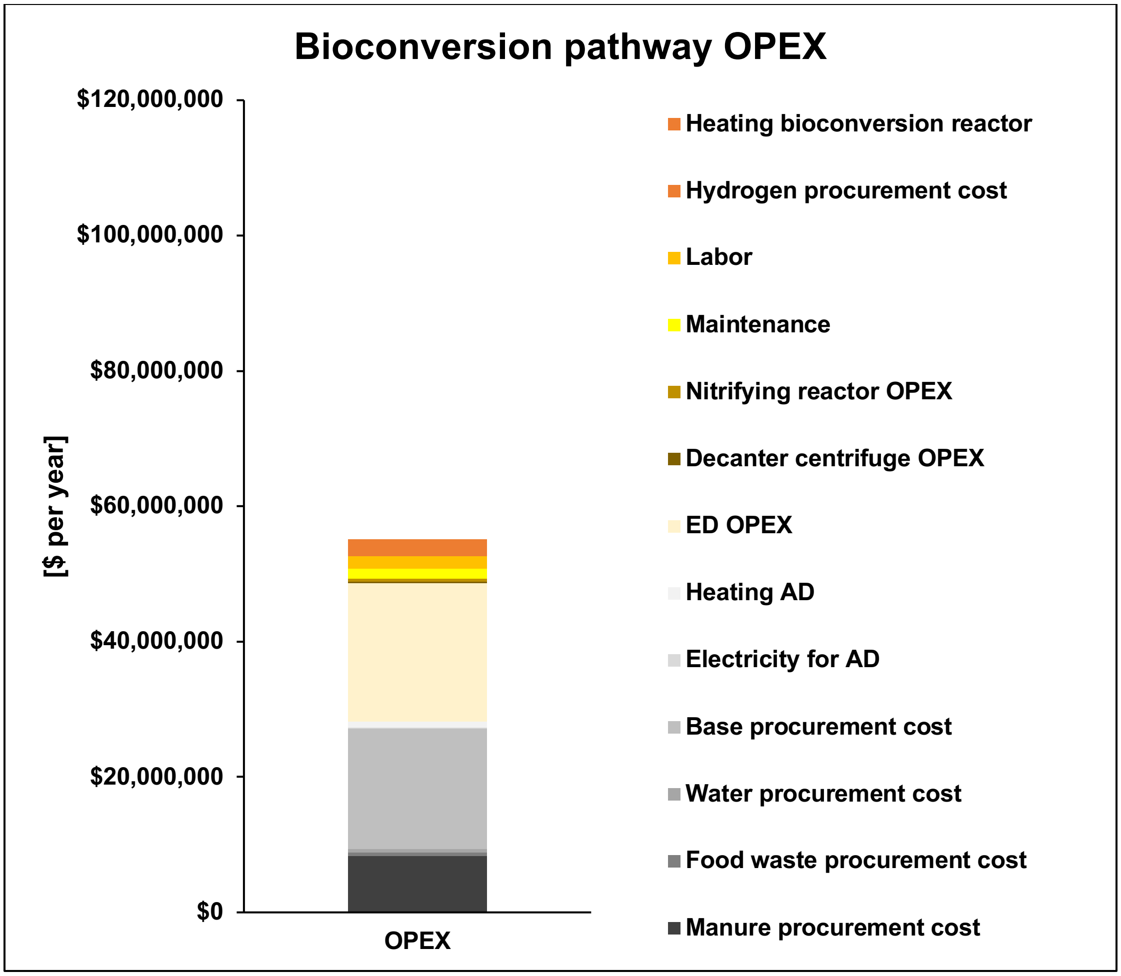


Figure A. 2. OPEX distribution for baseline n-butanol production by bioconversion of VFAs produced from AD of manure and FW. All OPEXs are expressed in $ per year. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: food waste; OPEX: operational expenditures; ED: electrodialysis; AD: anaerobic digestion; SLS: solid-liquid separation; VFA: volatile fatty acid)

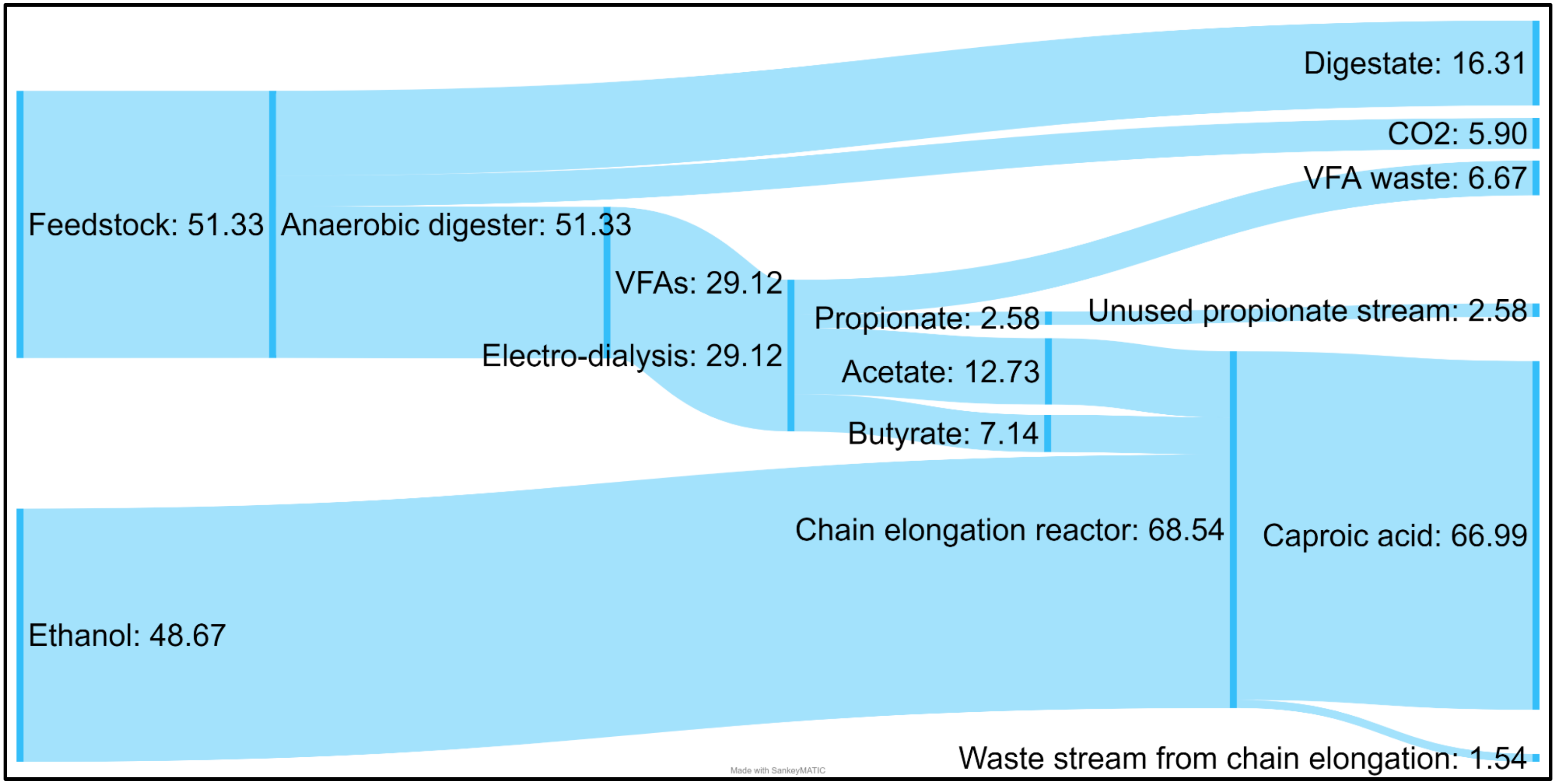


Figure A. 3. Sankey diagram for carbon flows baseline caproic acid production by chain elongation of VFAs produced from AD of manure and FW. All numbers are in percent. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: food waste; ED: electrodialysis; AD: anaerobic digestion; SLS: solid-liquid separation; VFA: volatile fatty acid)

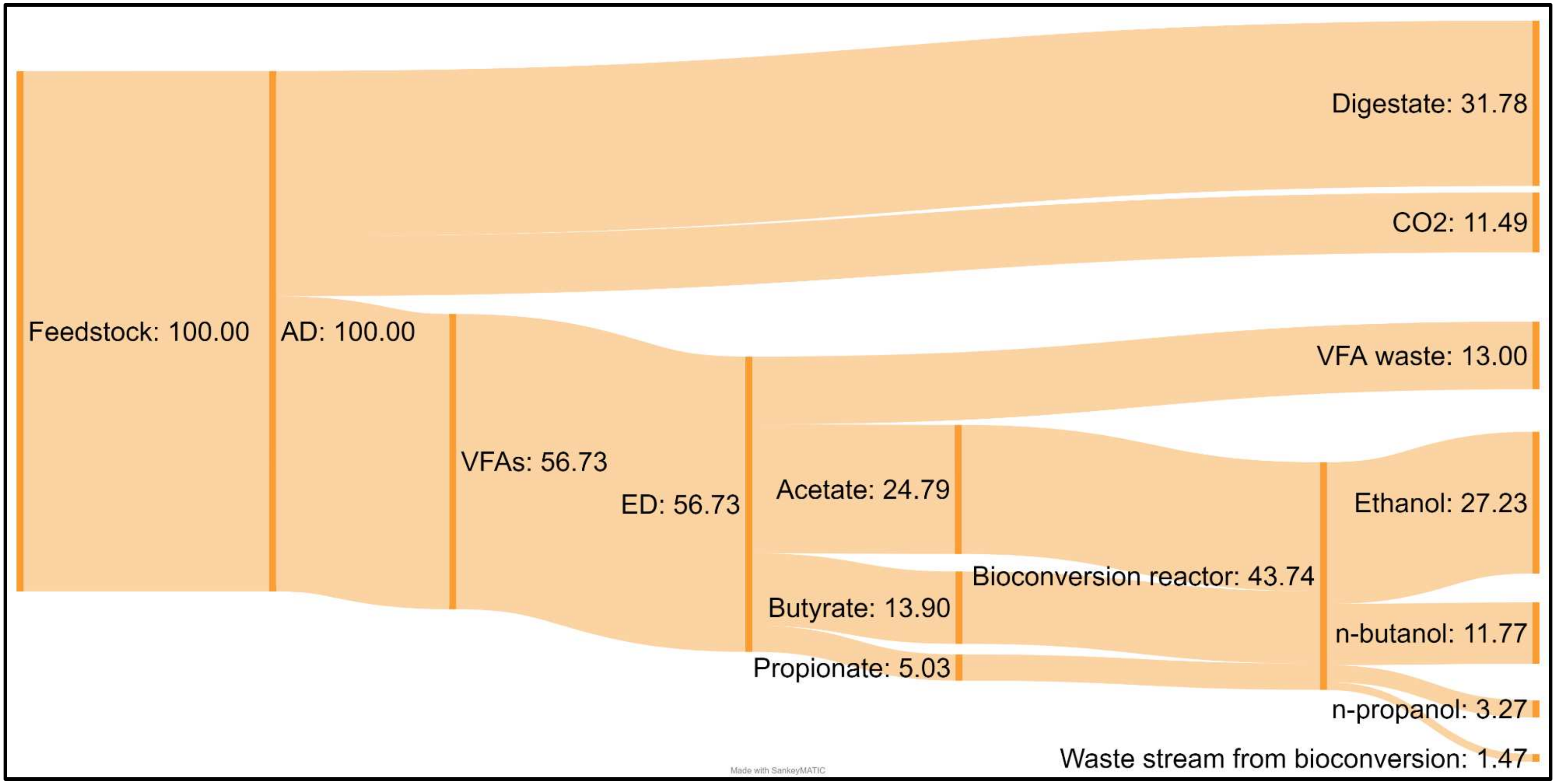


Figure A. 4. Sankey diagram for carbon flows baseline n-butanol production by bioconversion of VFAs produced from AD of manure and FW. All numbers are in percent. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: food waste; ED: electrodialysis; AD: anaerobic digestion; SLS: solid-liquid separation; VFA: volatile fatty acid)

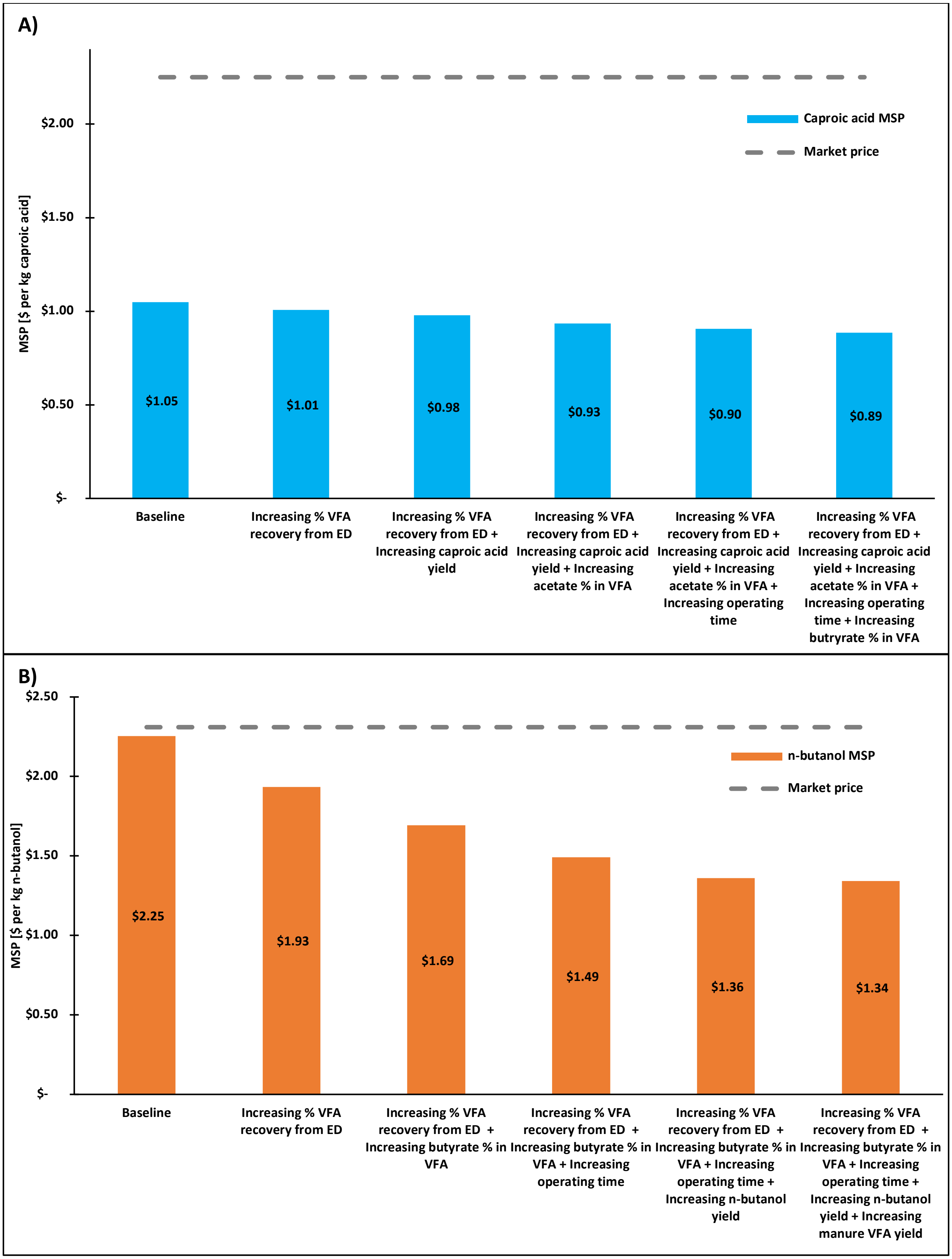
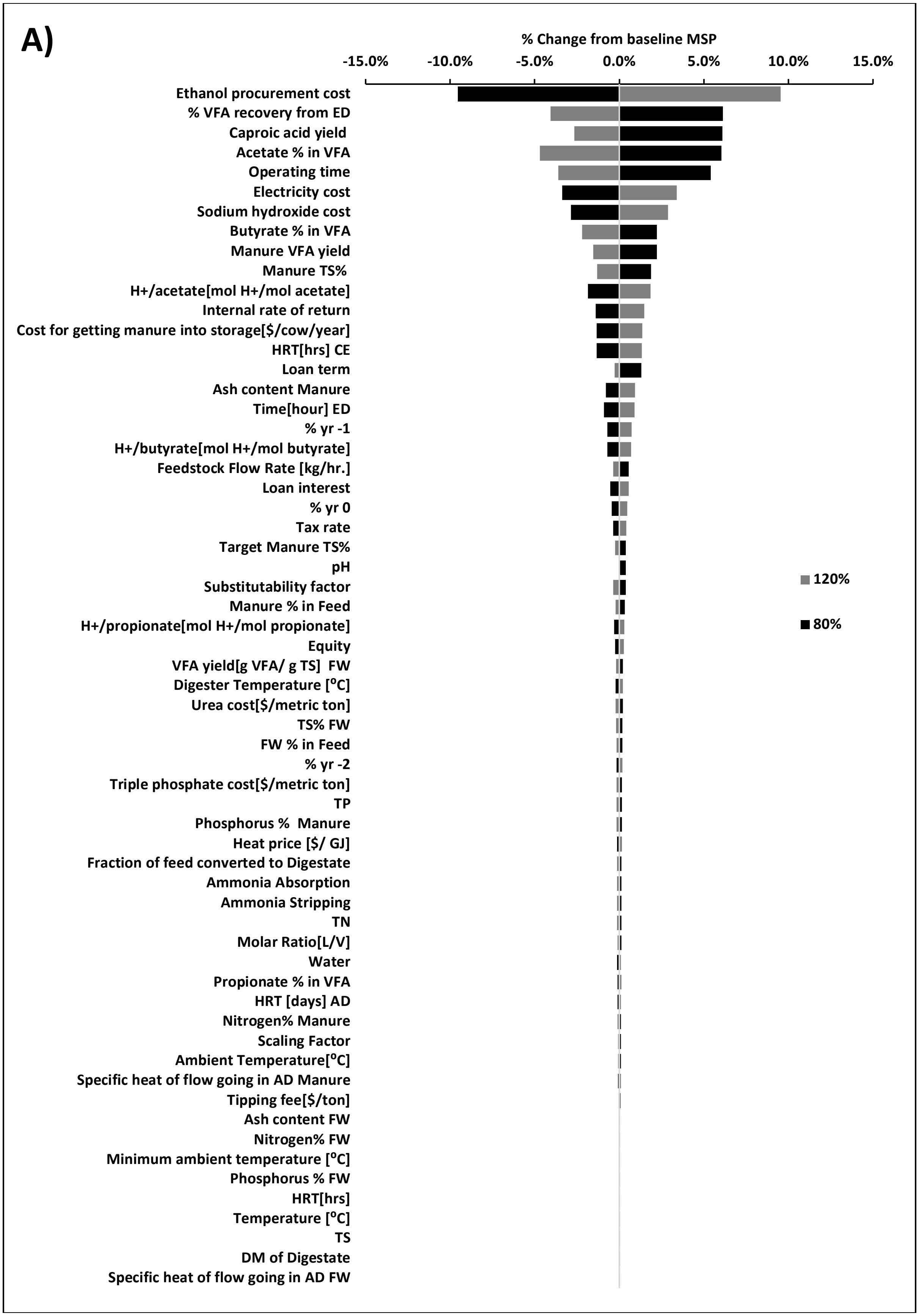


Figure A. 5. A) Optimistic scenarios in which the 5 of the most sensitive inputs are adjusted

by ±20% to reduce MSP for caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and FW. B) Optimistic scenarios in which the 5 of the most sensitive inputs are adjusted by ±20% to reduce MSP for n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and FW. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, Solid-Liquid Separation (SLS) of digestate and treatment of liquid digestate before land application. (FW: Food Waste; MSP: Minimum Selling Price; ED: electrodialysis; AD: anaerobic digestion; SLS: solid-liquid separation; VFA: volatile fatty acid)


A)
% Change from baseline MSP
-15.0%
-10.0%
-5.0%
0.0%
5.0%
10.0%
15.0%
Ethanol procurement cost
% VFA recovery from ED
Caproic acid yield
Acetate % in VFA
Operating time
Electricity cost
Sodium hydroxide cost
Butyrate % in VFA
Manure VFA yield
Manure TS%
H+/acetate[mol H+/mol acetate]
Internal rate of return
Cost for getting manure into storage[$/cow/year]
HRT[hrs] CE
Loan term
Ash content Manure
Time[hour] ED
% yr -1
H+/butyrate[mol H+/mol butyrate]
Feedstock Flow Rate [kg/hr.]
Loan interest
% yr 0
Tax rate
Target Manure TS%
pH
Substitutability factor
Manure % in Feed
H+/propionate[mol H+/mol propionate]
Equity
VFA yield[g VFA/ g TS] FW
Digester Temperature [°C]
Urea cost[$/metric ton]
TS% FW
FW % in Feed
% yr -2
Triple phosphate cost[$/metric ton]
TP
Phosphorus % Manure
Heat price [$/ GJ]
Fraction of feed converted to Digestate
Ammonia Absorption
Ammonia Stripping
TN
Molar Ratio[L/V]
Water
Propionate % in VFA
HRT [days] AD
Nitrogen% Manure
Scaling Factor
Ambient Temperature[°C]
Specific heat of flow going in AD Manure
Tipping fee[$/ton]
Ash content FW
Nitrogen% FW
Minimum ambient temperature [°C]
Phosphorus % FW
HRT[hrs]
Temperature [°C]
TS
DM of Digestate
Specific heat of flow going in AD FW
120%
80%

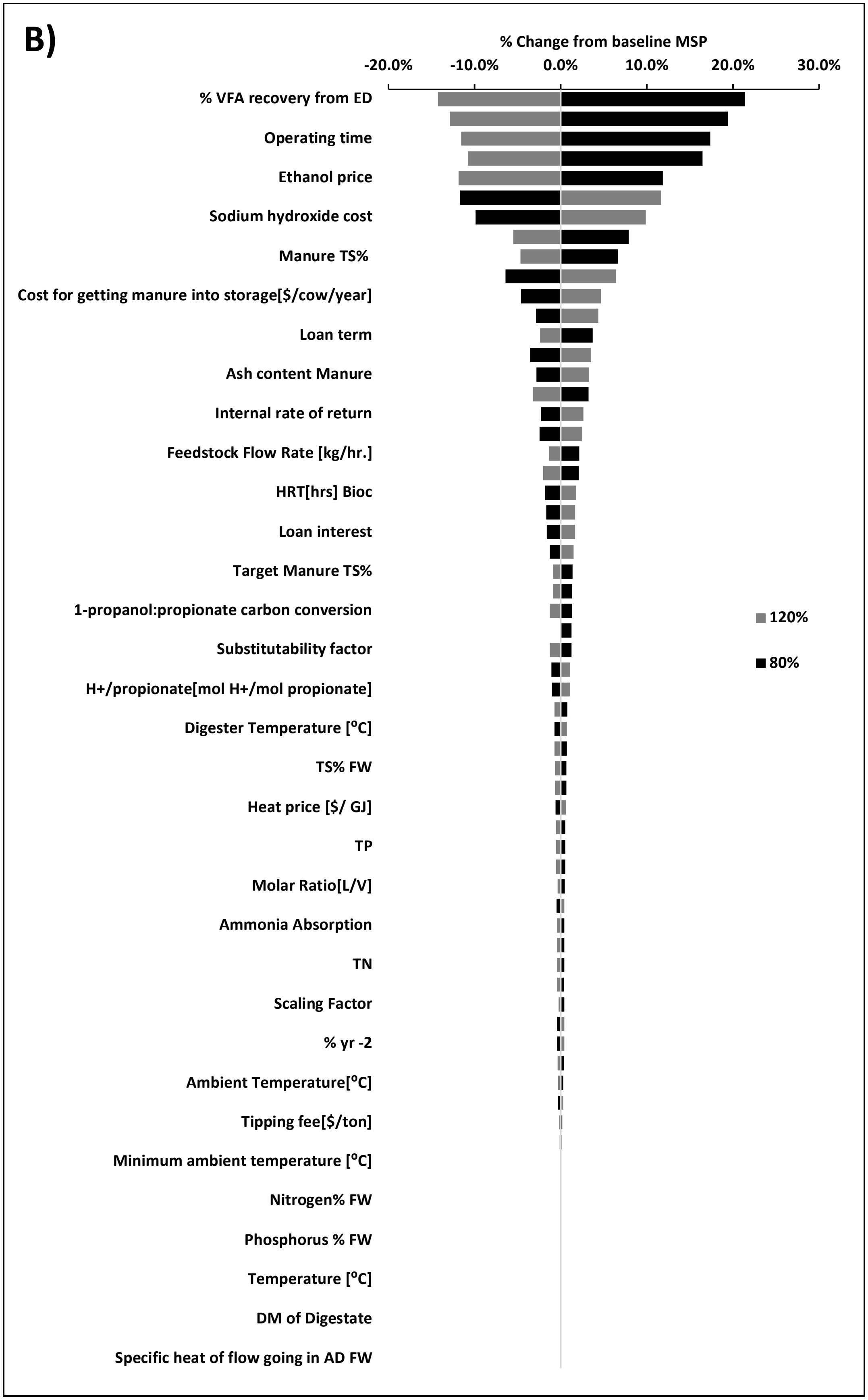
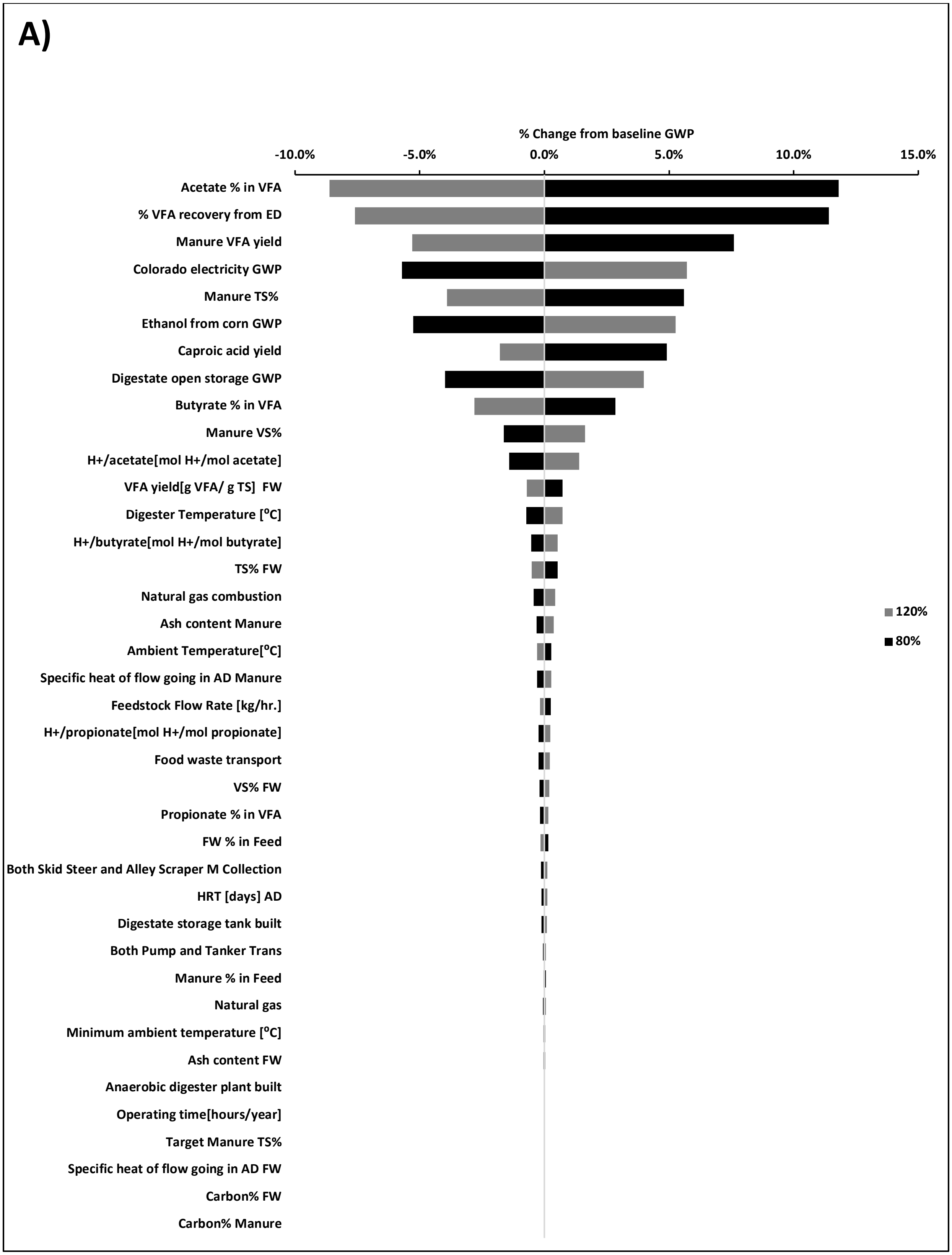

B)
% Change from baseline MSP
-20.0%
-10.0%
0.0%
10.0%
20.0%
30.0%
% VFA recovery from ED
Operating time
Ethanol price
Sodium hydroxide cost
Manure TS%
Cost for getting manure into storage[$/cow/year]
Loan term
Ash content Manure
Internal rate of return
Feedstock Flow Rate [kg/hr.]
HRT[hrs] Bioc
Loan interest
Target Manure TS%
1-propanol:propionate carbon conversion
Substitutability factor
H+/propionate[mol H+/mol propionate]
Digester Temperature [°C]
TS% FW
Heat price [$/ GJ]
TP
Molar Ratio[L/V]
Ammonia Absorption
TN
Scaling Factor
% yr -2
Ambient Temperature[°C]
Tipping fee[$/ton]
Minimum ambient temperature [°C]
Nitrogen% FW
Phosphorus % FW
Temperature [°C]
DM of Digestate
Specific heat of flow going in AD FW
120%
80%

Figure A. 6. A) All sensitive modeling parameters, with respect to MSP for a baseline scenario of caproic acid production from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) All sensitive modeling parameter, with respect to MSP for a baseline scenario of n-butanol production from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The black bars indicate the corresponding delta in MSP ($ per kg biochemical) for a 20% decrease in the input variable. The grey bars indicate the corresponding delta in MSP ($ per kg biochemical) for a 20% increase in the input variable. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. (FW: Food Waste; MSP: Minimum Selling Price; ED: Electro-Dialysis; VFA: Volatile Fatty Acid; TS: Total Solids; DM: dry matter; HRT: Hydraulic Retention Time; TN: total nitrogen; TP: total phosphorus)


A)
% Change from baseline GWP
-10.0%
-5.0%
0.0%
5.0%
10.0%
15.0%
Acetate % in VFA
% VFA recovery from ED
Manure VFA yield
Colorado electricity GWP
Manure TS%
Ethanol from corn GWP
Caproic acid yield
Digestate open storage GWP
Butyrate % in VFA
Manure VS%
H+/acetate[mol H+/mol acetate]
VFA yield[g VFA/ g TS] FW
Digester Temperature [°C]
H+/butyrate[mol H+/mol butyrate]
TS% FW
Natural gas combustion
Ash content Manure
Ambient Temperature[°C]
Specific heat of flow going in AD Manure
Feedstock Flow Rate [kg/hr.]
H+/propionate[mol H+/mol propionate]
Food waste transport
VS% FW
Propionate % in VFA
FW % in Feed
Both Skid Steer and Alley Scraper M Collection
HRT [days] AD
Digestate storage tank built
Both Pump and Tanker Trans
Manure % in Feed
Natural gas
Minimum ambient temperature [°C]
Ash content FW
Anaerobic digester plant built
Operating time[hours/year]
Target Manure TS%
Specific heat of flow going in AD FW
Carbon% FW
Carbon% Manure
120%
80%

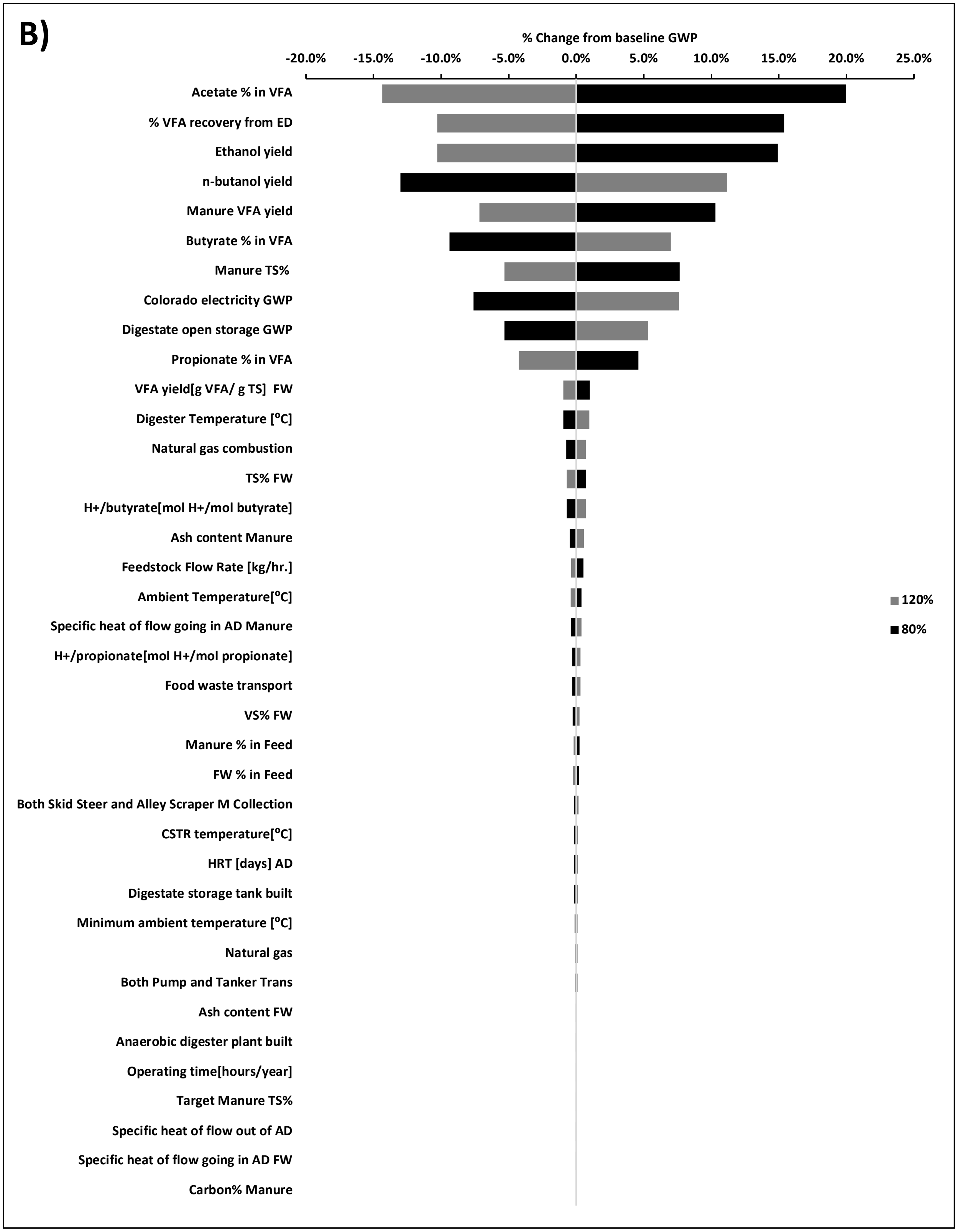


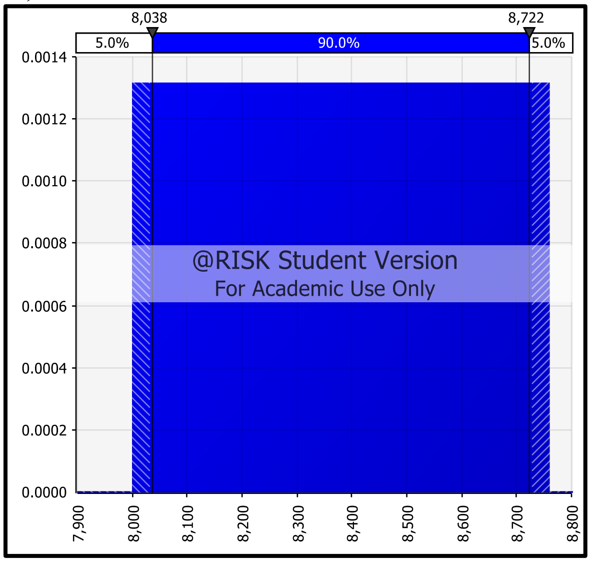
Figure A. 7. A) All sensitive modeling parameters, with respect to GWP for a baseline scenario of caproic acid produced from chain elongation of VFAs produced from anaerobic digestion of manure and food waste. B) All sensitive modeling parameter, with respect to

GWP for a baseline scenario of n-butanol produced from bioconversion of VFAs produced from anaerobic digestion of manure and food waste. The black bars indicate the corresponding delta in GWP (g CO_2-eq·$MJ_{biochemical}^{-1}$) for a 20% decrease in the input variable. The grey bars indicate the corresponding delta in GWP (g CO_2-eq·$MJ_{biochemical}^{-1}$) for a 20% increase in the input variable. The baseline scenario assumes the use of feedstock water homogenization, pH control in AD, ED to recover VFAs, SLS of digestate and treatment of liquid digestate before land application. Credits are ignored in the Monte Carlo analysis. (ED: Electro-Dialysis; VFA: Volatile Fatty Acid; FW: Food Waste; AD: Anaerobic Digester; GWP: Global Warming Potential; NG: Natural Gas; TS: Total solids; VS: Volatile solids)

Table A. 2. This table illustrates the lower impact an increase in yield causes to the minimum selling price compared to a decrease in yield.

Change in yield	-20%	0%	20%
Fixed Cost [$\$\cdot year^{-1}$]	100	100	100
Yield[$kg\cdot year^{-1}$]	8	10	12
MSP[$\$\cdot kg^{-1}$]	12.5	10.0	8.3
Percent change in MSP	25.0%	0.0%	-16.7%

A)



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8,722
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90.0%
5.0%
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
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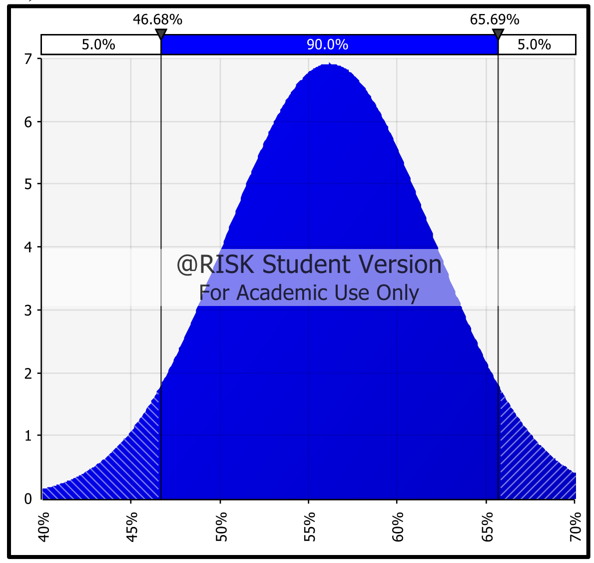
7,900
8,000
8,100
8,200
8,300
8,400
8,500
8,600
8,700
8,800

C)



46.68%
65.69%
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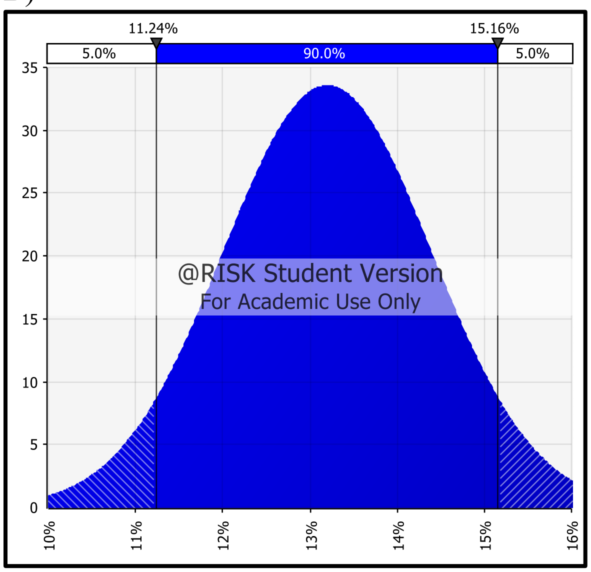
B)



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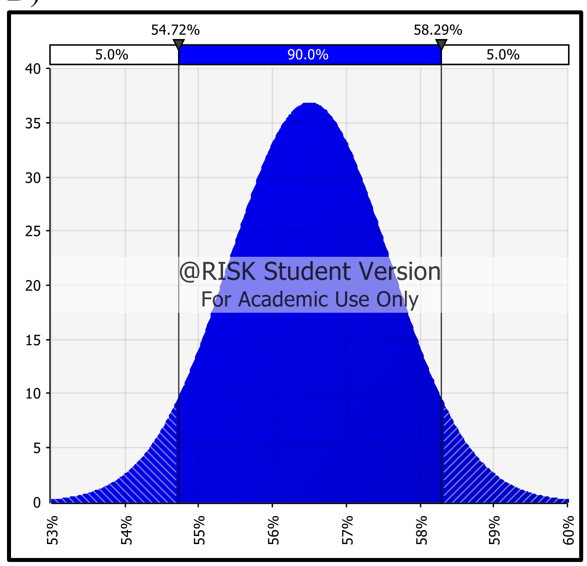

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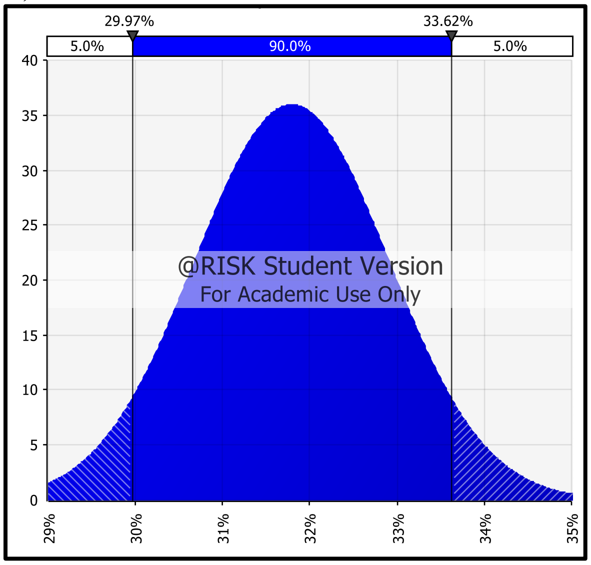
E)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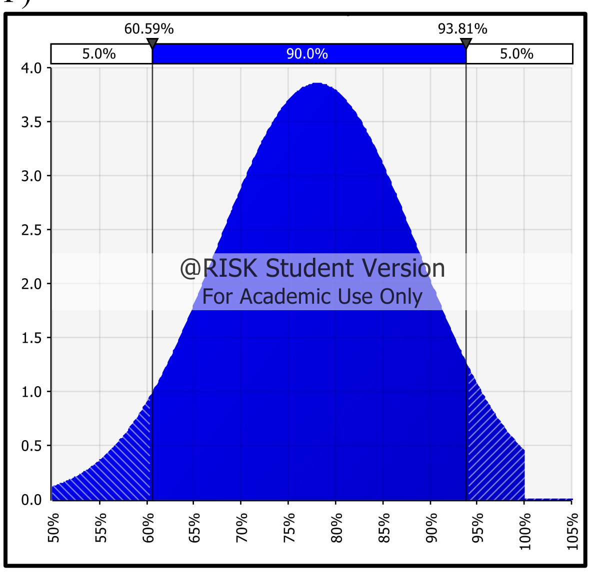
F)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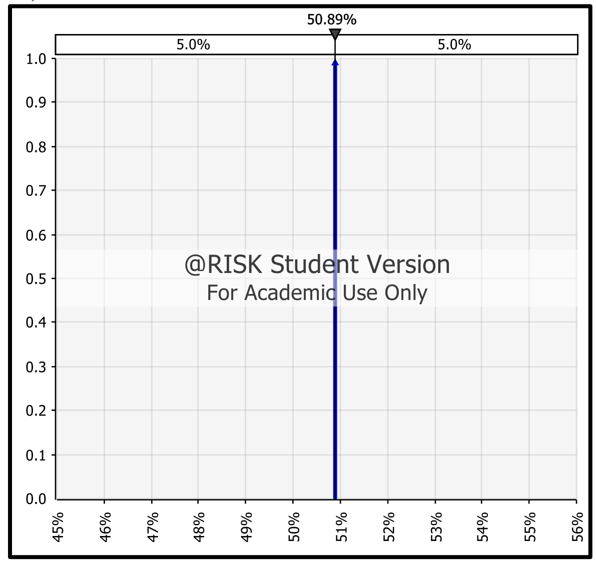
G)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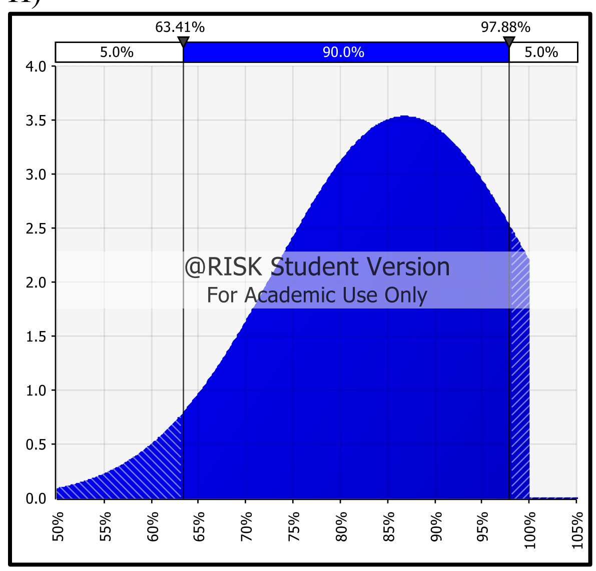
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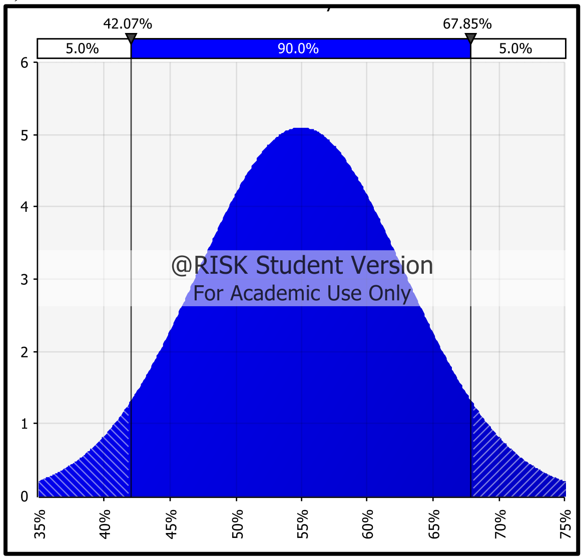
I)



J)

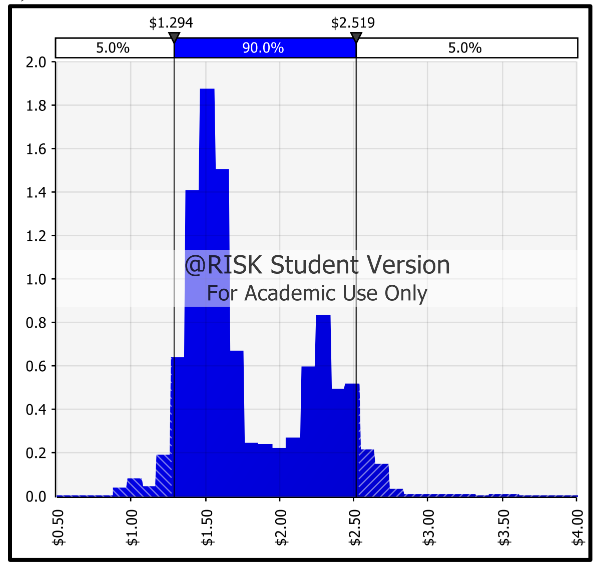


Figure A. 8. Distributions used for the Monte Carlo analysis of the minimum selling price and global warming potential for caproic acid and n-butanol production from VFAs produced in anaerobic digestion of wet wastes. A) Operating time B) Manure TS% C) Manure VFA yield D) Acetate percent in VFA E) Butyrate percent in VFA F) Percent VFA recovery in ED G) Caproic acid yield H) Ethanol yield in bioconversion I) n-butanol yield J) Ethanol cost (TS: Total Solids; VFA: Volatile Fatty Acid; ED: Electrodialysis)

LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
CAPEX	Capital Expenditure
CSTR	Continuous Stirred Tank Reactor
DCFROR	Discounted Cash Flow Rate Of Return
ED	Electrodialysis
FW	Food Waste
GWP	Global Warming Potential
HRT	Hydraulic Retention Time
LCA	Life Cycle Assessment
MSP	Minimum Selling Price
OPEX	Operational Expenditure
SLS	Solid-Liquid Separation
TEA	Techno-Economic Analysis
TS	Total Solid
VFA	Volatile Fatty Acid
VS	Volatile Solid