

Modeling and Analysis



Succinic acid production derived from carbohydrates: An energy and greenhouse gas assessment of a platform chemical toward a bio-based economy

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Abstract: Bio-based succinic acid has the potential to become a platform chemical, i.e. a key building block for deriving both commodity and high-value chemicals, which makes it an attractive compound in a bio-based economy. A few companies and industrial consortia have begun to develop its industrial production on a large scale. A life cycle assessment of different bio-based succinic acid production processes, based on dextrose from corn, was performed to investigate their non-renewable energy use (NREU) and greenhouse gas (GHG) emissions, from cradle-to-factory gate in Europe. Three processes were studied, i.e. (i) low pH yeast fermentation with downstream processing (DSP) by direct crystallization, (ii) anaerobic fermentation to succinate salt at neutral pH (pH7) and subsequent DSP by electrodialysis, and (iii) a similar process producing ammonium sulfate as co-product in DSP. These processes are compared to the production of petrochemical maleic anhydride, succinic acid, and adipic acid. Low pH yeast fermentation to succinic acid with direct crystallization was found to have significantly lower GHG emissions and NREU, compared to other fermentation routes and three petrochemical routes. However, the disparity in GHG emissions between this process and the electrodialysis process becomes less prominent if one considers a cleaner electricity mix than the current European production mix. Moreover, this study highlights that the allocation approach in corn wet milling and the succinic acid plant location strongly influence the results. Overall, the results suggest that low pH yeast fermentation with direct crystallization is the most beneficial process to bio-based succinic acid from an environmental perspective. © 2013 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: bio-based succinic acid, life cycle assessment, non-renewable energy use, greenhouse gas emissions, dextrose, maleic anhydride, adipic acid



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Introduction

ising atmospheric greenhouse gas (GHG) concentrations, volatile oil prices, security of supply, and the need to build a sustainable global economy are all strong incentives for the transition from today's fossil-fuelbased economy toward a bio-based economy. The development of highly efficient and cost-effective biorefineries is a prerequisite for such a bio-based economy. 1,2 The cost of producing conventional petrochemicals is often lower compared to bio-based compounds, due to optimization of the production processes over more than half a century. Producers of bio-based products have so far primarily targeted high value or specialty chemical markets. However, modern biotechnology allows the improvement of economics for bio-based building blocks for bulk applications, which forms a driver for investments in new biorefineries. In 2004, the US Department of Energy (DOE) published a report in which the 15 most promising sugar-derived products from an initial list of over 300 compounds are discussed.³ One of these products is a four-carbon dicarboxylic acid (C₄H₆O₄), known as succinic acid, which has been identified as one of the most important platform chemicals, also by Bechthold et al. Bozell and Peterson, 5 and experts convened in the BREW project.⁶

Today, the world market volume of succinic acid is relatively small at 15 000 tonnes per year. Succinic acid for industrial use is predominantly petrochemically produced from butane through catalytic hydrogenation of maleic acid or maleic anhydride (MAn).^{1,7} However, starting from high-value applications, bio-based succinic acid has the potential to gradually become a key building block for commodity chemicals,³ depending on the achievable cost reduction in the fermentation-based production from carbohydrates, next to other factors (e.g. technological progress in conversion to derivatives and the respective markets). Its promise lies in the ease of biotechnological production⁴ and in potentially many derivatives and applications, nowadays produced from petrochemicals.^{8,9} An important application of bio-based succinic acid could be the production of commodity chemical 1,4-butanediol (1,4-BDO), which is a starting material for tetrahydrofuran (THF) and γ-butyrolactone (GBL). Moreover, the specialty chemical *n*-methylpyrrolidinone (NMP) can be produced from GBL and bio-based succinic acid could potentially substitute petrochemical adipic acid in the production of polyester polyols to polyurethanes. ¹⁰ Moreover, it could also be used as feedstock for the production of polybutylene succinate (PBS, a biodegradable polymer used for flexible film applications), for which the market

is expected to grow due to a rising interest in biodegradable products.¹¹ Furthermore, there are opportunities for the use of succinic acid for the production of detergents, surfactants, pigments, resins, biodegradable solvents, food, and pharmaceutical products⁷ next to other applications, for example plasticizers (Smidt M, Reverdia, 2012, pers. comm.).

A few companies and industrial consortia have begun to develop the industrial production of bio-based succinic acid (Table 1). A technical breakthrough in the production process of bio-based succinic acid using low pH yeast fermentation with subsequent DSP by direct crystallization is expected to result in overall improved economics and environmental footprint.¹² In order to prove and exploit this advantage, Reverdia (joint venture Roquette

Table 1. Status of the industrial production of bio-based succinic acid. 11,37-39

	Capacity (ktonne/year)				
Producer	SA	1,4-BDO	PBS	Start-up	Location
Reverdia ¹	10			Q4 2012	Cassano Spinola, Italy
Myriant ²	14			Q2 2013	Lake Providence, Louisiana
Myriant ³	77			Q1 2014	Lake Providence, Louisiana
BASF, Purac ⁴	10			2013	Barcelona, Spain
BioAmber	3			Q1 2010	Pomacle, France
BioAmber, Mitsui ²	30			Q4 2014	Sarnia, Ontario, Canada
BioAmber, Mitsui ³	50			2016	Sarnia, Ontario, Canada
BioAmber, Mitsui	65	50		2014	Thailand
BioAmber, Mitsui	65	50			United States, Brazil
PTT MCC Biochem	36		20		Rayong, Thailand

Figures are updated in June 2013. Compound abbreviations: SA = succinic acid, 1,4-BDO = 1,4-butanediol, PBS = polymer polybutylene succinate.

¹Joint venture DSM/Roquette.

²Start-up capacity.

³Full capacity.

⁴Joint venture BASF and Purac, which is a subsidiary of CSM.

and DSM) started production in a commercial plant of about 10 kt p.a. in December 2012 (Table 1). In order to provide quantitative information on the environmental performance of various process routes Reverdia commissioned Utrecht University to prepare a comprehensive life cycle assessment (LCA) study, which forms the basis of this publication. This paper presents the findings on non-renewable energy use (NREU) and climate change for three bio-based processes and compares the results to three petrochemical counterparts. This study aims to answer the following questions:

- 1. What is the impact on NREU and climate change of succinic acid production based on dextrose from corn in comparison to three petrochemical counterparts?
- 2. What is the influence of choices made regarding allocation approach and plant location on the results for bio-based succinic acid?
- 3. What are the most contributing sub-processes in the process chain of bio-based succinic acid?

Methodology

LCA is a widely accepted methodology to assess the environmental performance of services and products. LCA studies are applied for communication purposes, for process or product chain optimization, and for support in decision-making where environmental considerations are taken into account. The LCA methodology is standardized in the ISO 14040 series by the International Organization of Standardization (ISO). ^{13,14} This study is performed according to these standards.

Scope definition

The functional unit, i.e. the basis for comparison, is one kg of high-grade bio-based succinic acid (≥99.5 wt-% pure). Product quality and impurity profile for all commercial bio-based succinic acid is assumed to qualify for polymer application, i.e. similar purity levels as petrochemical succinic acid. The system boundary is set to cradle-to-factory gate (from extraction of raw materials up to and including the production of succinic acid, excluding transport to customer). The life cycle stages after the factory gate are not included, since succinic acid is a chemical intermediate with a wide range of applications and therefore a wide range of process pathways. This study is performed with the most recent process and design data for bio-based succinic acid production from Reverdia's operating demonstration plant. Data on the petrochemical process is taken from Ecoinvent¹⁵ (based on MAn), industry sources

(petrochemical succinic acid), and the UNFCCC national inventory submission database (Germany, the UK, France, and Italy)¹⁶, combined with data from ICIS¹⁷ (adipic acid). The feedstock data is based on a study of European dextrose production from corn starch.¹⁸ The geographical coverage is the European Union (EU), while the influence of this choice on the results is evaluated by means of a sensitivity analysis on plant location. The biogenic carbon embodied in succinic acid is deducted from the calculated gross GHG emissions (while the time period of storage is not considered), as recommended by the European Commission's Lead Market Initiative, 19 GHG Protocol Initiative, 20 and PAS2050, 21 for cradle-to-factory gate systems.²² This study covers the impact categories of NREU and climate change. Its characterization factors are taken from impact method 'Cumulative Energy Demand' (v1.08) and 'IPCC 2007 GWP 100a' (v1.02), respectively.

Allocation approach

The definition of allocation is 'Partitioning the input or output flows of a process or a product system between the product system under study and one or more other product systems'. 13 Environmental impacts of multi-output processes are partitioned for processes shared with other product systems. Where allocation is required in this study, the prioritized allocation procedure defined by ISO 14044 is followed, ¹⁴ i.e. at first avoiding allocation either by subdivision or system expansion and secondly partitioning based on physical relationships (mass allocation). The applied allocation approaches are shown in Table 2, with the preferred allocation approach (default) marked in bold. Applying system expansion for the corn wet milling (CWM) process can lead to rather extreme results, ¹⁸ which makes the choice for subdivision combined with mass allocation more appropriate. For the ammonium sulfate (AS) process to succinic acid and the combined heat and power (CHP) plant, system expansion is preferred since large-scale processes for producing AS and power are being operated and suitable data are available.

Plant location

The influence of the plant location on the results is evaluated by means of a sensitivity analysis, including the USA, Brazil, and China. The background processes for the supply of utilities are modified based on the location, while the same production process is assumed. The studied cases are shown in Table 3. Two feedstocks are evaluated: dextrose from corn for Europe, the USA, and China and sucrose from sugarcane for Brazil (Center-South region).

Table 2. Applied allocation approaches for the corn wet milling process, the gate-to-gate ammonium
sulfate process to succinic acid, and the on-site combined heat and power production process.

Processes	Allocation through partitioning				Avoiding allocation
Corn wet milling (feedstock)	Sub- division	Main process	Black box: Mass allocation	Black box: Economic allocation	System expansion
Gate-to-gate succinic acid (co-product ammonium sulfate) ¹				Black box: Economic allocation	System expansion
Combined heat and power					System expansion
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¹For the conversion of dextrose to succinic acid, only the ammonium sulfate process is subject to allocation due to the formation of a co-product.

Table 3. Process configurations studied for sensitivity analysis on plant location.

Location	Feedstock of fermentable sugar	Fuel for on-site CHP	Process abbreviation
Europe (EU)	CH corn	Gas-fired	EU Gas-CHP
Unites States (US)	US corn	Gas-fired	US Gas-CHP
Unites States (US)	US corn	Coal-fired	US Coal-CHP
Brazil (BR)	Sugarcane	Gas-fired	BR Sugarcane
China (CN)	CH corn ¹	Coal-fired	CN Coal-CHP
1			

¹The corn cultivation figures for Switzerland (CH) are used due to a lack of data on corn cultivation in China.

These carbohydrates currently represent the most important feedstocks for bio-based material production. ²³ The inventory for sucrose from sugarcane is based on data from Ecoinvent and the study of Seabra *et al.* ²⁴

Process descriptions

Table 4 provides an overview of the studied bio-based succinic acid production processes and the three petrochemical counterparts. The flow diagrams and process data of the bio-based succinic acid production processes are given in Fig. 1 and Table 5, respectively. The data sources are listed in Table 6.

System delimitation decisions resulted in exclusion of some processes.* Figure 1 shows that the micro-organisms are first propagated on fermentable sugar, nutrients, and ammonia. They are then mixed with a fermentable sugar feedstock in a fermenter, where a fermentation process produces the succinic acid. In the bacterial, as well as in the yeast-based succinic acid production process, a small amount of CO_2 is absorbed in the fermentation process for the metabolism of micro-organism, leading to the required enzyme (PEP carboxykinase and/or pyruvate carboxylase). All three processes have an on-site digester

and CHP plant. After the separation of biomass by centrifugation or microfiltration and the separation of mother liquor from the crystallization process, both streams are converted to biogas in the digester. The biogas substitutes part of the natural gas taken from the grid to fuel the on-site CHP. The CHP is dimensioned according to the steam requirements of the plant, with electricity being the co-product. Data on CHP come from real industrial CHP facilities (Table 6). The amount of co-generated electricity depends on the electricity-to-steam ratio of the CHP plant (0.47 for a gas-fired and 0.19 for a coal-fired CHP). The plant consumes the co-generated electricity and any excess electricity is fed back into the grid for which the process receives credits based on the avoided electricity production mix. If the CHP is not producing enough electricity to

- *(1) The transport of dextrose hydrolyzate to the succinic acid production facility is negligible since dextrose and succinic acid are produced on the same site.
- (2) The transport of chemicals to the succinic acid plant. The partly unknown and numerous locations of bio-based succinic acid production facilities and their chemical suppliers make it difficult to include it in this comparative study. The AS process is slightly favored due to this decision, because the required total transport service (related to the inputs of ammonia and sulfuric acid) is somewhat larger for this process than for the other two processes. However, the difference has been estimated at only 0.03 kg $\rm CO_2$ eq./kg succinic acid and is hence negligible (the estimation is based on the 'Transport, lorry >32t,RER' process from Ecoinvent, with average EURO3-5, assuming 100 km of transport).
- (3) The production of fermentation nutrients is assumed negligible (Van de Graaf M, DSM Biotechnology Centre, 2012, pers. comm.).
- (4) The production of activated carbon (the amounts consumed are minimal and its impacts are estimated at less than 1% impact) and micro-, ultra- and nanofiltration membranes for the electrodialysis process.
- (5) The salt stream leaving the system boundary is disposed of as diluted effluent: 0.057 kg salt/kg succinic acid, based on the salt mass balance.

Table 4. Succinic acid production processes studied.					
BIO-BASED PROCES	SSES				
	Process abbreviation ¹	Fermentation technology	Downstream processing		
Succinic acid	BioSA-DC	Low pH yeast-based to succinic acid	Direct crystallization		
	BioSA-ED	Neutral-pH bacteria-based to succinate salt	Electrodialysis		
	BioSA-AS	Neutral-pH bacteria-based to succinate salt	Ammonium sulfate as a co-product		
PETROCHEMICAL P	ROCESSES				
	Process abbreviation ²	Process description			
Maleic anhydride	Pchem MAn	Direct oxidation of <i>n</i> -butane in a fluidized bed	d process ¹⁵		
Succinic acid	Pchem SA	Catalytic hydrogenation of maleic anhydride			
Adipic acid ³ Pchem AA Oxidation of a mixture of cyclohexanol and cyclohexanone by nitric acid					
4					

¹Bio-based succinic acid produced through low pH yeast fermentation with DSP by direct crystallization (BioSA-DC), anaerobic fermentation to succinate salt at neutral pH (pH7) and subsequent DSP by electrodialysis (BioSA-ED), and a similar process producing ammonium sulfate as co-product in DSP (BioSA-AS).

²Pchem MAn = petrochemical maleic anhydride; Pchem SA = petrochemical succinic acid; Pchem AA = petrochemical adipic acid.

³A weighted average of adipic acid production in EU-27 for 2010 is calculated using capacity data from ICIS¹⁷, N₂O emission data from UNFCCC, ¹⁶ and a characterization factor of 298 kg CO₂ eq./kg N₂O from IPCC. ⁴⁰

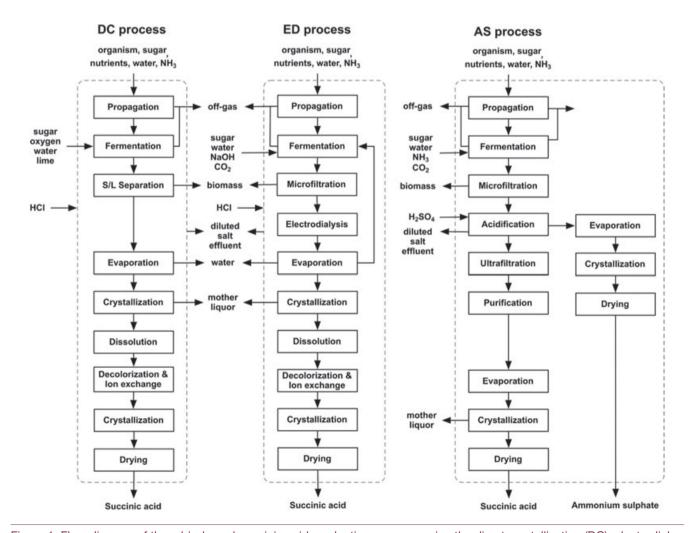


Figure 1. Flow diagram of three bio-based succinic acid production processes, i.e. the direct crystallization (DC), electrodialysis (ED), and ammonium sulfate (AS) process.

Table 5. Process data for 1 kg of bio-based succinic acid production by three different process routes.¹

	Direct crys- tallization	Electro- dialysis ²	Ammonium sulfate ³	Unit		
Input						
Materials						
Carbon dioxide	-	0.289	0.292	kg		
Process water	31.00	29.20	32.48	kg		
Total titrants	0.128	0.132	1.645	kg		
Energy						
Total steam	3.114	3.177	6.497	kg		
Electricity	1.672	3.267	1.995	kWh		
Steam from biogas ⁴	-0.606	-0.596	-0.656	MJ		
Electricity credit	-	-	-0.203	kWh		
Output						
Materials						
Mother liquor	-	1.299	1.430	kg		
Biomass (dry wt.)	-	0.098	0.107	kg		
Waste sludge	0.001	0.001	0.001	kg		
Ammonium sulfate	-	-	1.607	kg		
Succinic acid	1.000	1.000	1.000	kg		
Emissions to air (gas–fired CHP – share of emissions attributed to steam) ⁵						
Carbon dioxide	0.376	0.387	0.876	kg		
Sulfur dioxide	1.936	1.993	4.511	mg		
Nitrogen oxides	0.319	0.328	0.743	g		
Emissions to air (gas–fired CHP – share of emissions attributed to electricity) ⁵						
Carbon dioxide	0.257	0.263	0.537	kg		
Sulfur dioxide	1.326	1.353	2.767	mg		
Nitrogen oxides	0.219	0.223	0.456	g		

¹Process data for three fermentative process routes to succinic acid were kindly provided by DSM Biotechnology Centre (Van de Graaf M, 2012, pers. comm.).

cover the demand, the remaining electricity requirement is taken from the grid.

Direct crystallization process

The low pH yeast fermentation with DSP by direct crystal-lization (DC) is shown in Fig.1(a). In this process, hydrochloric acid (HCl) is added for softening and mild acidification of the process liquor. In the evaporation process the dissolved product stream is concentrated by evaporation using heat provided by mechanical vapor recompression (MVR). In the crystallization process the succinic acid crystals are separated from the mother liquor, which still contains 7 wt-% dissolved succinic acid. As already mentioned, the mother liquor is digested to produce biogas. The product is then purified to form a high-grade succinic acid through polish treatment, recrystallization and drying.

Electrodialysis process

The anaerobic fermentation to succinate salt at neutral pH (pH7) and subsequent DSP by electrodialysis (ED) is shown in Fig.1(b). After fermentation, the broth is clarified using microfiltration membranes. The succinate salt ($C_4H_4Na_2O_4$) from the fermentation broth is concentrated and converted to succinic acid by means of electrodialysis, after which similar process steps are applied as for the DC process.

Ammonium sulfate process

The anaerobic fermentation to succinate salt at pH7 and co-production of AS in the DSP is shown in Fig. 1(c). Ammonia (NH₃) and sulfuric acid (H₂SO₄) are fed to the fermentation and acidification process, respectively, in relatively large quantities compared to the other process configurations (a factor 35 more ammonia and 16 times more H₂SO₄ compared to HCl). Distinctive features of the AS process are the separation by ultra- and nanofiltration and the co-production of AS according to the chemical reaction: $2 \text{ NH}_3 + \text{H}_2 \text{SO}_4 \boxtimes (\text{NH}_4)_2 \text{SO}_4$. It is assumed that the AS is separated from the succinic acid by chromatography (cation exchange), which results in a relatively dilute co-product stream. To dry the co-produced AS, the AS process requires relatively large amounts of steam compared to the other processes. Evaporation is typically done in a thermal evaporator, since MVR is too expensive due to a high boiling point elevation of salt solutions. As a result of the higher steam requirement, the gas-fired CHP is dimensioned larger and produces excess electricity

²The power required for electrodialysis and pressure drop compensation is taken into account, while the impact of membrane consumption is considered negligible. Besides, potential impacts from pre-concentrating the alkali-recycle in the process are also neglected.

³Consumption of ultra- and nanofiltration membranes is not included in the scope of this process.

⁴Biogas is fed to the gas-fired CHP on-site to displace natural gas from the grid.

 $^{^5\}text{The}$ emissions allocated to steam (64.5%) and electricity (35.5%) for the gas-fired CHP are based on the system expansion approach. The steam production from biogas is subtracted from the total steam requirement. The emissions from the remaining steam requirement are given in the table above. The CO_2 emissions originating from biogas combustion are not included, since these emissions are biogenic and therefore considered neutral.

Table 6. Data sources of bio-based succinic acid production from dextrose.					
	Process input	Description	Ref.		
Input	Grid electricity	Electricity production mix (medium voltage) ¹	34		
	Gas-fired CHP	CHP in Belvidere, New Jersey, DSM ²			
	Coal-fired CHP	Real industrial CHP facility in China ²			
	Dextrose	Dextrose hydrolyzate (32% dry solids)	18		
	Biogenic CO ₂	From an ethanol fermentation plant ³	41		
	Bottled CO ₂	Carbon dioxide liquid, at plant/RER	15		
	Process water	Tap water, at user/RER	15		
	Ammonia	Ammonia, liquid, at regional storehouse/RER	15		
	Sulfuric acid Sulfuric acid, liquid, at plant/RER		15		
	Ca(OH) ₂	Lime, hydrated, loose, at plant/CH ⁴	42		
	HCI	Hydrochloric acid, 30% in H ₂ O, at plant/RER	15		
	NaOH	Sodium hydroxide, 50% in H ₂ O, production mix, at plant/RER	15		
Output	Waste sludge	Disposal, raw sewage sludge, to municipal incineration/CH ⁴	43		
	(NH ₄) ₂ SO ₄	Ammonium sulfate, as N, at regional storehouse/RER ⁵	35		

¹The weighted electricity production mix of Europe is used as default. For the location-dependent sensitivity analysis, the electricity production mix of the United States (US), Brazil (BR), and China (CN) is used respectively.

(while the other two processes draw complementary power from the grid).

Petrochemical processes

The chemistry for the production of 1,4-BDO, THF, and GBL from succinic acid is similar to the conversion starting from MAn,³ since MAn is converted to succinic acid as in situ intermediate. Petrochemically produced 1,4-BDO from MAn is widely practiced, 25 which makes MAn a suitable reference petrochemical for bio-based succinic acid. 6,26,27 MAn is nowadays predominantly produced by catalytic oxidation of C₄ hydrocarbons. Process data from the Ecoinvent unit process 'maleic anhydride from the direct oxidation of n-butane, at plant' were used to determine the NREU and GHG emissions. 15 Inventory data from other sources for MAn may lead to deviating results, due to differences in the amount of steam co-produced. The reaction enthalpies from Eqns (1) and (2) show that the oxidation of *n*-butane is strongly exothermic.³⁰ As a result, high-pressure steam of 50 bar is produced as a coproduct,²⁹ with a corresponding temperature of ~264°C. The amount of co-produced steam is strongly dependent on the achieved yield for the catalytic oxidation of

n-butane (Eqn (1)). Lower yields result in more unreacted n-butane, which increases the amount of steam produced in the incineration unit for waste gases (Eqn (2)).

$$C_4H_{10} + 3.5 O_2 \boxtimes C_4H_2O_3 + 4 H_2O \quad \Delta H_r = -1,236 \text{ kJ/mol}$$
(1)

$$C_4H_{10} + 6.5 O_2 \boxtimes 5 H_2O + 4 CO_2 \quad \Delta H_r = -2,656 \text{ kJ/mol}$$
 (2)

Theoretically, the reaction from Eqn (1) can produce 5.3 kg steam per kg MAn † of 50 bar, based on 1.105 kg or 19.0 mol n-butane input and a yield of 63%. The recovery of the 37% unreacted n-butane is substantially more difficult than with benzene as feedstock; therefore waste gases are incinerated. This produces an additional 1.7 kg steam (and it causes an additional amount of in 1.24 kg CO $_2$ emissions ‡), which

²CHP data were kindly provided by DSM Biotechnology Centre (Van de Graaf M, 2012, pers. comm.).

³The dehydrated and compressed CO₂ stream comes directly from an integrated ethanol fermentation plant, which costs are in the range of 6-12 US\$/tonne. ⁴¹ Here, it is assumed that all costs represent electricity costs, with a market price of 0.10 US\$/kWh, resulting in 0.06 kWh/kg CO₂.

⁴The Ecoinvent unit processes of Switzerland (CH) are used in case of lacking EU data (RER).

⁵The conversion of ammonium sulfate to N is taken into account using 0.212 kg N/kg (NH₄)₂SO₄.

 $^{^{\}dagger}\textsc{Based}$ on a closed system and a specific enthalpy of 2,794 kJ/kg of saturated steam.

[‡]These emissions are caused by the complete oxidation of the unreacted n-butane (7.0 mol/kg MAn) based on the reaction stoichiometry of Eqn (2). Based on stoichiometric quantities the reported value of 4.21 kg CO₂ emissions in Ecoinvent (Chemicals report, Table 50.4) was corrected into 1.24 kg CO₂ emissions, in consultation with the author.¹⁵

adds up to 7.0 kg steam per kg MAn. 15 However, an efficiency of 90% is assumed for transferring the heat released in the reactor and incinerator unit to the steam-pipe system (Roes AL et al., forthcoming). Moreover, only an estimated 80% of the co-produced steam is utilized in practice (Bosch H, DSM, February 5, 2013, pers. comm.), resulting in net 5.0 kg steam per kg of MAn. System expansion is applied to the MAn production process to be consistent with the AS process, instead of applying economic allocation, as is done in Ecoinvent. For the substituted system, the fuel requirement of the boiler (here: 100% natural gas) is 2.39 MJ natural gas per kg steam and is calculated using a simplified steam model, developed by Roes AL, et al. (forthcoming).** Since energy integration has a greater impact on MAn production costs than scale, 31 it is assumed that MAn production facilities are located on industrial sites where steam is an important utility. At such sites, closed steam systems are common (Bosch H, DSM, October 10, 2012, pers. comm.) and therefore assumed for calculations with the simplified steam model.

The process from MAn to succinic acid consists of a catalytic hydrogenation reaction followed by hydration (MAn + $H_2 \boxtimes$ succinic anhydride + $H_2 \bigcirc \boxtimes$ succinic acid). The succinic acid solution is concentrated and cooled to enable crystallization of the succinic acid. The solids crystals are recovered by centrifugation and dried. The aggregated data for this process are obtained from industry sources. However, if MAn is replaced by bio-based succinic acid to produce 1,4-BDO, drying of succinic acid is not relevant. Therefore, the impact results for petrochemical succinic acid in liquid form lies somewhere between the results for MAn and petrochemical succinic acid.

Impact assessment results

In this section, the process data are translated into environmental impacts, using the allocation approaches from Table 2, highlighted in bold. The impact on NREU and climate change is presented in Fig. 2. The DC process shows a significantly lower impact on NREU (51% and 38%) and climate change (92% and 67%) compared to the ED and AS

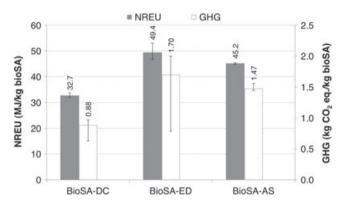


Figure 2. Non-renewable energy use (NREU) and green-house gas (GHG) emissions of bio-based succinic acid production by the direct crystallization (DC), electrodialysis (ED) and ammonium sulfate (AS) process route, using a European electricity production mix. The error bars represent the range in impacts from national electricity production mixes within Europe. Regarding NREU the lower values represent Italy, while for GHG emissions the lower values represent France.

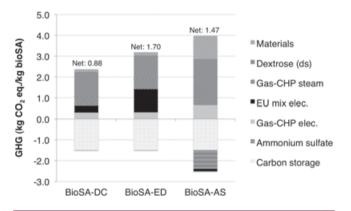


Figure 3. Breakdown of sub-process contributions for greenhouse gas emissions of biobased succinic acid production from dextrose.

process, respectively. However, if one considers a cleaner electricity mix (e.g. the French instead of European production mix) the disparity in GHG emissions between the DC and ED process becomes less prominent, as shown by the error bars in Fig. 2. A GHG emission breakdown into its sub-processes for bio-based succinic acid, shown in Fig. 3, explains this observation.^{††}

The ED process requires relatively large amounts of electricity. However, only one-third of its electricity demand

[§]Ecoinvent approach results in 2.37 kg CO₂ eq./kg MAn.¹⁵

^{**}Steam model based on a closed steam cycle. Assuming a boiler efficiency of 89%⁶, a steam-pipe distribution efficiency of 92.5%⁶, a heat transfer efficiency of 90% from steam-pipe to process, and a condensate recovery fraction of 75% (minimal for bulk processes) (Bosch H, DSM, May 3, 2012, pers. comm.).

^{††}Biogenic carbon embodied in succinic acid (through uptake during cultivation of corn) is deducted from the calculated gross GHG emissions.

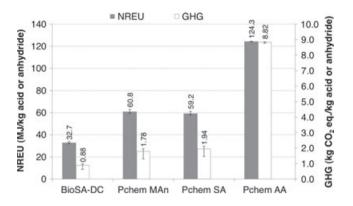


Figure 4. Non-renewable energy use (NREU) and green-house gas (GHG) emissions of bio-based succinic acid production from dextrose (i.e. the DC process) and three petrochemical counterparts, i.e. maleic anhydride (Pchem MAn), succinic acid (Pchem SA), and adipic acid (Pchem AA), using a European electricity production mix.

is covered by the on-site CHP, while it is nearly two-thirds in the case of the DC process (Fig. 3). The higher emission intensity of grid electricity compared to the on-site CHP (\sim 0.5 compared to \sim 0.3 kg CO₂ eq./kWh) and the higher electricity demand of the ED process result in 0.79 kg CO₂ eq. higher emissions compared to the DC process. These emissions are significantly lowered when the French electricity production mix (\sim 0.1 kg CO₂ eq./kWh) is considered. Compared to the ED and DC process the AS process shows significantly higher GHG emissions related to the materials used and the steam requirements (Fig. 3). Moreover, the carbon storage in succinic acid (displayed as negative emissions in Fig. 3) originates from the carbon uptake during cultivation of corn and amounts to \sim 1.5 kg CO₂ per kg of succinic acid.

Figure 4 shows the impact on NREU and climate change of the DC process compared to three petrochemical counterparts. Butane-based MAn production has a nearly 90% higher NREU and approximately a factor of two higher GHG emissions compared to the DC process. The error bars in Fig. 4 indicate a large range of GHG emissions, i.e. 1.29-1.96 kg CO₂ eq. per kg MAn, depending on the electricity mix. MAn-based succinic acid production shows slightly higher GHG emissions and even lower NREU results compared to 'Pchem MAn'. The reason is that only 0.85 kg MAn is required per kg of succinic acid. Furthermore, Fig. 4 shows a great disparity between the DC process and adipic acid produced from petrochemicals. The NREU and GHG emissions for adipic acid are, respectively, by a factor of 3.8 and 10.0 higher compared to the DC process. NREU and GHG emission savings are 74% and 90%, respectively, per kg of feedstock when

petrochemical adipic acid is replaced by bio-based succinic acid, produced by the DC process, for the production of polyurethanes.

The land use per tonne of succinic acid derived from corn is 0.22 hectare (ha), which is slightly higher than the land use of bio-based PLA (\sim 0.18 ha/tonne) and significantly lower than bio-based PE (\sim 0.46 ha/tonne), both derived from corn. ^{18,32}

Discussion

Allocation method - CWM process

A sensitivity analysis is performed on alternative allocation approaches for the CWM process. The results for 1 kg of succinic acid are shown in Fig. 5. The allocation approaches are described in detail in Tsiropoulos et al.¹⁸ The subdivision approach (default) from Fig. 5 has the second lowest GHG emissions (0.88 kg CO₂ eq./kg succinic acid). If, instead of subdivision, system expansion is applied with soybean originating from Brazil, the GHG emissions are only 0.78 kg CO₂ eq./kg succinic acid (compared to 1.14 kg CO₂ eq./kg succinic acid in the US scenario; higher impact due to clearly smaller substitution credit). While in the USA all land used is arable land, this is not the case in Brazil. As a consequence, large amounts of GHG emissions are associated with the transformation of primary forest to arable land for soybean cultivation in Brazil, albeit for 3.2% of the land use.³³ The system expansion approach for the CWM process involves large uncertainties of up to ~20% for climate change, due to assumptions made for land use before soybean cultivation, which depends on the country of origin of soybean substitution

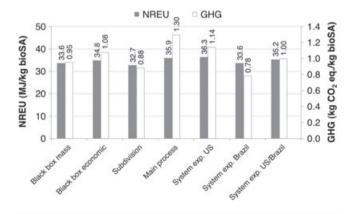


Figure 5. Non-renewable energy use (NREU) and greenhouse gas (GHG) emissions of bio-based succinic acid production from dextrose (i.e. the DC process) using different allocation approaches.

products. The uncertainty associated with the system expansion approach does not make it a suitable approach in this study. The black box approach based on mass allocation results in 8% higher GHG emissions, compared to subdivision. This increase is caused by the relatively high natural gas requirement for drying the CWM co-products (steepwater, germ, fiber, and gluten) per unit of mass. The black box approach based on economic allocation leads to 22% higher GHG emissions, since dextrose represents about 78% of the total economic output of the CWM process. The main process approach shows 47% higher GHG emissions compared to subdivision, due to the allocation of all emissions resulting from corn handling, corn steeping and germ, fiber, and gluten separation to the main product dextrose.

Allocation method – ammonium sulfate process

Ammonium sulfate (AS) is formed in the fermentation to succinic acid in one of the processes (Fig. 1). As shown in Table 2, the preferred allocation approach (No. 1 in Fig. 6) for the AS process is system expansion. The effect of this choice on the GHG emission results is studied by analysing four other possible allocation approaches (Fig. 6). Number 2, 3, and 5 represent a uniform allocation approach for the entire life cycle, i.e. system expansion, subdivision followed by mass allocation, and economic allocation, respectively. Moreover, No. 4 is a combination

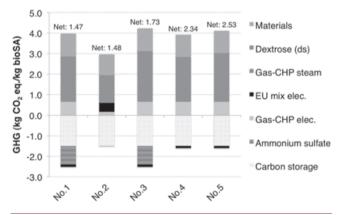


Figure 6. Greenhouse gas (GHG) emissions of bio-based succinic acid production from dextrose (i.e. the AS process) using alternative allocation approaches for the CWM and succinic acid production process. No. 1: default, No. 2, 3 and 5: uniform allocation approach for the entire life cycle, i.e. system expansion, subdivision, and economic allocation, respectively. No. 4: subdivision for the CWM process and economic allocation for the succinic acid production process.

of subdivision for the CWM process and economic allocation for the succinic acid production process.

The GHG emission results for one kg of bio-based succinic acid increase by 1% and 18% if priority is given to uniformity of respectively subdivision with mass allocation and system expansion throughout the life cycle of foreground processes (Fig 6: 1 \(\times 2\) and 1 \(\times 3\), respectively). However, if the system expansion approach for the succinic acid production process is changed into partitioning through economic allocation, an increase of 59% in GHG emissions is observed (Fig. 6: 1 🛭 4). The large difference in market value between succinic acid and AS could justify the allocation of inputs and outputs according to the economic value of both products. The market price of AS amounts to 0.15-0.31 US\$/kg (Van de Graaf M, DSM Biotechnology Centre, 2012, pers. comm.), while today's spot price for succinic acid ranges from 3 to 9 US\$/kg, depending on its purity and application (Smidt M, Reverdia, 2012, pers. comm.). If priority is given to uniformity of economic allocation procedure throughout the life cycle, the GHG emissions increase by 72% (Fig. 6: 1 ∑ 5). The price of succinic acid is expected to decrease once its production volume is expanded. As a consequence, the burden allocated to succinic acid would be lowered. However, the effect is small, since halving the average price of succinic acid only results in a 2% reduction of GHG emissions. To summarize, the choice made regarding allocation approach strongly influences the impact on climate change for the AS process, i.e. the GHG emissions vary from 1.5 to 2.5 kg CO₂ eq. per kg succinic acid. For this study, the selected allocation approach for the AS process, i.e. subdivision for CWM followed by system expansion for succinic acid production, has the lowest GHG emissions of all approaches (Fig. 6).

Plant location

The process configurations for different plant locations are given in Table 3. The modeling results of the plant location sensitivity analysis are shown in Fig. 7. It shows that the difference in GHG emissions between the DC and ED process becomes smaller for Brazil, and larger for the USA and China. This observation is explained by the difference in emission intensity of a country's electricity production mix. Since the ED process is more power intensive compared to the DC process (Fig. 3), larger differences in GHG emissions are observed for countries with a higher emission intensity of their electricity production mix.

When comparing the different plant locations for the DC process, some differences are observed. The US plant with

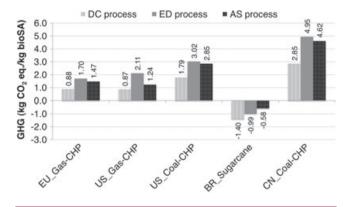


Figure 7. Net Greenhouse gas emissions of biobased succinic acid production from dextrose for different plant locations (Europe, United States, Brazil and China) and CHP fuel sources (gas- or coal-fired).

a gas-fired CHP shows a 2% reduction in GHG emissions while the electricity production mix of Europe (502 g CO₂) eq./kWh) is cleaner than that of the US (771 g CO₂ eq./ kWh).³⁴ The higher emissions attributed to 'grain maize IP, at farm/CH' (544 g CO₂ eq./kg), compared to 'corn, at farm/US' (433 g CO₂ eq./kg) compensate slightly more than this difference.³⁵ The US plant with a coal-fired CHP shows gross GHG emissions which are 1.4 times higher compared to the EU plant, caused by the higher carbon content of coal compared to natural gas and secondly, by its significantly lower power to steam ratio (0.19 for a coal-fired CHP, compared to 0.49 for gas-fired). Therefore, about 80% of the required electricity is taken from the grid in the USA, compared to 37% for the gas-fired CHP scenario in Europe. Due to the higher GHG emission intensity of grid power in the USA compared to Europe, this results in a clearly higher contribution to climate change

compared to the EU plant. A feedstock switch of dextrose from corn to sucrose from sugarcane (Fig. 7: EU Gas-CHP ☐ BR Sugarcane) demonstrates a high environmental improvement potential, due to the bagasse and electricity surpluses as co-products, 24 resulting in negative GHG emissions for sucrose. The gate-to-gate analysis to succinic acid is based on the Brazilian electricity mix. This mix includes a high share of hydropower, which is reflected by a 54% decrease in GHG emissions resulting from grid electricity use compared to the EU plant. The Chinese (CN) plant with a coal-fired CHP shows gross GHG emissions which are approximately 1.8 times higher compared to the EU plant (Fig. 7: EU Gas-CHP

© CN Coal-CHP), caused by its significantly lower power to steam ratio, the higher GHG emission intensity of coal (compared to gas) and Chinese grid electricity (1,180 g CO₂ eq./kWh).³⁴

Contribution analysis

Figures 8 and 9 show a contribution breakdown to climate change of sub-processes in the life cycle of bio-based succinic acid (i.e. the DC process) and its feedstock, respectively. Figure 8(a) shows the total contribution of dextrose production, while for Figure 8(b) the dextrose contribution is broken down in utilities, corn, transport, and chemicals. The dextrose production is responsible for about half of all GHG emissions (Fig. 8(a)). The second largest contributor, with 19% of the emissions, is steam production from the on-site CHP. The electricity production from the on-site CHP (13%) has an equal contribution as grid electricity (13%). The required materials contribute merely 6% to the total GHG emissions. They include the production of decarbonized process water, ammonia, lime, HCl, and NaOH, of which HCl is the largest contributor (48%).

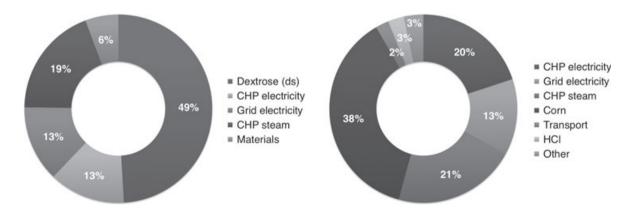


Figure 8. Sub-process contributions to greenhouse gas emissions of bio-based succinic acid production from dextrose (i.e. the DC process), with an aggregated contribution for dextrose production (left) and a breakdown for dextrose production only (right).

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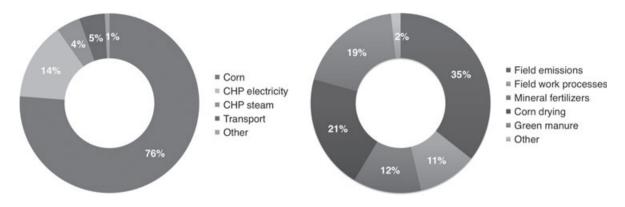


Figure 9. Sub-process contributions to greenhouse gas emissions of dextrose production from corn, with an aggregated contribution for corn production (left) and a breakdown for corn production only (right).

Figure 9(a) shows the breakdown for dextrose production. The corn production is clearly dominating its overall climate change impact (76%). The gas-fired CHP utilities contribute 18% and corn transport from field to CWM facility only 5%. The remainder ('other') consists of compressed air, wastewater treatment plant emissions, and materials. The contribution of materials (sulfur dioxide (SO₂), sodium hydroxide (NaOH), and decarbonized process water) in the CWM process is very small (0.4%). The corn-steeping process requires low concentrations of SO₂ in a water solution to form an acidic environment. NaOH is used to control pH levels of the starch slurry in the preparation tanks. 36

Figure 9(b) shows the breakdown of emissions from corn production. The most important contributions come from direct field emissions (35%), corn drying (21%), and green manure (19%). The direct field emissions contribute 13% to the overall emission profile of succinic acid. These emissions are predominantly caused by emissions of nitrous oxide (N₂O) as an intermediate of the denitrification process $(NO_3^- \boxtimes N_2)$ and a by-product of the nitrification process $(NH_4^+ \boxtimes NO_3^-)$. The corn-drying process has a significant contribution of nearly 8% in the production of succinic acid (i.e. the DC process). Therefore, using location specific corn moisture data before and after drying is recommended. In this study, the assumed moisture content of harvested and stored corn is 39% and 14%, respectively. 35 The drying process evaporates 0.41 kg H₂O per kg corn through an air heater that runs on light heating oil. ‡‡ Modeling with a natural gas fired air heater will lower the GHG emission results, due to its lower carbon intensity.

Conclusions

In this study, the impact on NREU and climate change of succinic acid production derived from carbohydrates is investigated in comparison to three petrochemical counterparts. The low pH yeast fermentation process with DSP of direct crystallization (i.e. the DC process) was found to have a significantly lower impact on NREU (51% and 38%) and climate change (92% and 67%) compared to the electrodialysis (ED) and ammonium sulfate (AS) process, respectively. However, the disparity in GHG emissions between this process and the ED process becomes less prominent if one considers a cleaner electricity mix than the current European production mix. Moreover, the NREU and GHG emissions of the DC process compared to three petrochemical counterparts are a factor of 1.9–3.8 and 2.0–10.0 lower, respectively.

By means of a sensitivity analysis, this study has highlighted that the allocation approach in the CWM process strongly influences the modeling results. When giving priority to avoid allocation, the system expansion approach for CWM involves large uncertainties of up to ~20% for climate change. The uncertainties arise from the assumptions made for land use before soybean cultivation, which depends on the country of origin of soybean substitution products. The uncertainty associated with the system expansion approaches for the CWM process does not make it a suitable approach for this study. Therefore, the subdivision approach is combined with mass allocation for the CWM process, following the ISO allocation procedure. This study also highlights that the benefits of the DC process are increased, compared to the AS process, if a different allocation approach is used. The ranking is influenced by the allocation approach only for the ED and AS process.

^{‡‡}Formula: $W_{evap} = (W_e - W_i) / (W_i - 1.00) \approx 0.41 \text{ kg H}_2\text{O} / \text{kg corn; } W_{evap} =$ water evaporated (kg/kg product); $W_i / W_e =$ at the outset/end of the drying process (% moisture content).³⁵

Moreover, this study has highlighted that the plant location (Europe, the United States, Brazil, and China) strongly influences the results. This is explained by differences in electricity production mix, available feedstock, and fuel for the on-site CHP. Installing a plant in Brazil has demonstrated a large improvement potential, due to a feedstock switch of dextrose from corn to sucrose from sugarcane, while installing a plant in China significantly increases the environmental burden of the succinic acid life cycle, due to a fuel switch from natural gas to coal for the on-site CHP

The main contributors (environmental hot spots) are utilities, direct field emissions and corn drying in the dextrose production process. Overall, the results suggest that low pH yeast fermentation with direct crystallization is the most beneficial process to bio-based succinic acid from an environmental perspective.

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