# Greening two chemicals with one bio-alcohol: environmental and economic potential of dehydrogenation to hydrogen and acids

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# Supporting information

# Contents

# S1 Functional unit and system boundaries

## S1.1 Functional unit

The goal of this study is to calculate the environmental potential of four dehydrogenation routes to produce 1 kg of hydrogen and the corresponding stoichiometric amount of co-produced acids. The functional unit is chosen because hydrogen is the common product in the four dehydrogenation routes.

## S1.2 System boundaries

For the dehydrogenation routes and the benchmarks, we perform a cradle-to-grave assessment. The system boundary of the dehydrogenation route is limited to the stoichiometric chemical reaction, so it only accounts for entering feed streams and exiting product streams in the foreground system. The system boundary of the benchmark technology consists of the separated production of hydrogen and the production of acid. Benchmark technologies include raw materials, production, and transport to the market in the foreground system. In the fossil benchmark scenario, fossil benchmark technologies are selected. In the green benchmark scenario, green benchmark technologies are selected. The system boundaries also include the background processes for the supply of chemicals, utilities, and infrastructure of the foreground system inventories.

# S2 Selection of dehydrogenation reactions and benchmarks

We screen the IEA Bioreport [1] that lists 65 C1-C12 bio-chemicals with near-term market potential to find suitable dehydrogenation routes for the case study. First, we filter available bio-alcohols from the report as feedstocks for dehydrogenation routes. Next, we perform stoichiometric dehydrogenation reactions on the filtered bio-alcohols. We choose water as a co-reactant in each route as one relevant example of dehydrogenation [2], and because water is widely available. We select tap water by default, since there are no limitations on water impurities

to the authors knowledge. Dehydrogenation reactions were even performed in wastewater treatment [3].

Then, we evaluate the availability of the produced acids by stoichiometric dehydrogenation in the IEA Bioreport. Hereby, we select nine dehydrogenation routes (Table S1). We set the availability of bio-alcohols in the report (marked as 'pipeline' or 'growing' potential) as a cut-off criterion. Otherwise, feedstock availability could become a bottleneck to the dehydrogenation of bio-alcohols at a large scale. Hereby, we discard dehydrogenation of bio-based n-butanol.

Next, we search for life cycle inventories of the bio-alcohol feedstocks in the literature, which are required to perform an LCA. Moreover, we search for available fossil and green benchmark technologies for hydrogen and co-produced acids. In particular, an industrial-scale fossil benchmark is required to compare state-of-the-art technologies. Therefore, we introduce the availability of fossil benchmarks with a detailed LCI as a cut-off criterion. The life cycle inventories for bio-alcohols, hydrogen, and co-produced acids are selected from available databases and the literature if processes are unavailable in the databases. All bio-alcohols, except for ethylene glycol, are found in the ecoinvent database [4] or in a harmonized study of sugar-based bio-chemicals by Winter et al. [5]. Therefore, we discard ethylene glycol as dehydrogenation feedstock. We assume that sugar can be fermented to 1,2-propanediol, in the same manner as described by Winter et al. for sugar fermentation to 1,3-propanediol, arguing that the atoms are identical from a stoichiometric perspective and have a similar molecular structure. We find fossil benchmarks for acetic acid, formic acid, and lactic acid in the ecoinvent database version 3.9. Succinic acid can directly substitute fossil-based adipic acid [6]. We discard 3-hydroxypropionic acid and malonic acid since fossil benchmarks are unavailable. The screening results in four dehydrogenation routes that serve as a case study.

*Table S1: Dehydrogenation route candidates with final selection for the case study.*

| Alcohol Feedstocks | Acids Products |
|---|---|
| **Selected dehydrogenation routes** | |
| Methanol | Formic acid |
| Ethanol | Acetic acid |
| Propylene glycol (1,2-propanediol) | Lactic acid |
| 1,4-butanediol | Succinic acid |
| **Discarded dehydrogenation routes** | |
| Ethylene glycol | Glycolic acid |
| Ethylene glycol | Oxalic acid (from glycolic acid) |
| 1,3-propanediol | 3-Hydroxypropionic acid |
| (1,3-propanediol) | Malonic acid (from 3-Hydroxypropionic acid) |
| n-butanol | Butyric acid |

We calculate the reaction enthalpies of the selected dehydrogenation routes (Table S2). The reaction enthalpies indicate that the selected dehydrogenation routes are endothermic.

*Table S2: Reaction enthalpies of dehydrogenation routes per functional units.*

| Aspen Plus (NRTL-RK, 1 bar, 298 K, feedstock conversion 100%, stoichiometric reactor) | |
|---|---|
| Bio-acid co-produced with 1 kg hydrogen | Heat Duty Isothermal Stoichiometric Reactor in MJ |
| Formic acid | 32 |
| Acetic acid | 27 |
| Succinic acid | 19 |
| Lactic acid | 23 |

# S3 Life cycle inventories

We take the LCIs directly from the ecoinvent 3.9 database or build them from data in the

literature with activities from database. We select global (GLO) market activities in ecoinvent if

they are available. Otherwise, we select rest-of-world (RoW) market activities. If market

activities are unavailable, we select single processes with the location GLO or RoW.

## S3.1 Dehydrogenation routes

The life cycle inventories of the dehydrogenation routes are based on the mass balances resulting from stoichiometric reactions to produce 1 kg of hydrogen.

*Table S3: Stoichiometric dehydrogenation reactions with 100 % yields.*

| Target co-product acid | Chemical reactions | Material Flows | Mass flow in kg per 1 kg hydrogen | Activity in ecoinvent version 3.9 |
|---|---|---|---|---|
| Formic acid | $CH_3OH + H_2O \rightarrow$ $CHOOH + 2\,H_2$ | Methanol from wood chips | 7.95 | RoW: market for methanol from biomass |
| | | Tap water | 4.5 | RoW: market for tap water |
| | | **Formic acid** | **11.4** | |
| Acetic acid | $C_2H_5OH + H_2O \rightarrow$ $CH_3COOH + 2\,H_2$ | Ethanol from sugarcane | 11.43 | GLO: ethanol, without water, in 99.7% solution state, from fermentation |
| | | Tap water | 4.5 | RoW: market for tap water |
| | | **Acetic acid** | **14.9** | |
| Lactic acid | $C_3H_8O_2 + H_2O \rightarrow$ $C_3H_6O_3 + 2\,H_2$ | 1,2-propanediol from sugar fermentation [7][1] | 18.9 | GLO: market for glucose, 37.0 kg |
| | | | | RoW: market for oxygen, liquid, 11.9 kg |
| | | | | RoW: heat production, wood chips from industry, at furnace 300kW, 280.9 MJ |
| | | | | RoW: electricity production, wind, 1-3MW turbine, onshore, 0.8 kWh |
| | | Tap water | 4.5 | RoW: market for tap water |
| | | **Lactic acid** | **22.4** | |
| Succinic acid | $C_4H_{10}O_2 + 2\,H_2O \rightarrow$ $C_4H_6O_4 + 4\,H_2$ | Butanediol from sugar fermentation [7][2] | 11.2 | GLO: market for glucose, 22.4 kg |
| | | | | RoW: market for tap water, 0.308 kg |
| | | | | RoW: heat production, wood chips from industry, at furnace 300kW, 44.8 MJ |
| | | | | RoW: electricity production, wind, 1-3MW turbine, onshore, 6.2 kWh |
| | | Tap water | 4.5 | RoW: market for tap water |
| | | **Succinic acid** | **14.7** | |

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[1] Assumption that 1,2-propanediol can be produced the same way as 1,3-propanediol
[2] End-of-life CO2 emissions are included to account for the molecular difference in carbon compared to adipic acid

## S3.2 Fossil co-product benchmarks

The fossil-based co-products are directly selected from the ecoinvent database.

*Table S4: Fossil benchmark LCIs selected in the ecoinvent database, version 3.9.*

| Product | Activity name in ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|
| Formic acid | market for formic acid | RoW | kg | 11.4 |
| Acetic acid | acetic acid, without water, in 98% solution state | GLO | kg | 14.9 |
| Lactic acid | market for lactic acid | GLO | kg | 22.4 |
| Adipic acid | market for adipic acid | GLO | kg | 14.7 |
| Hydrogen | hydrogen production, steam reforming | RoW | kg | 1 |

## S3.3 Bio-based co-product benchmarks

We select green hydrogen from wind-powered electrolysis because it has the lowest climate change footprint [8] and represents the most competitive green hydrogen route.

We take harmonized life cycle inventories for the glucose-based lactic acid and succinic acid benchmarks from one literature reference [5]. The remaining green benchmarks come from individual references. The life cycle inventories of the green benchmarks (Table S5-S9) are assembled by using existing activities from ecoinvent version 3.9. Heat and electricity activities are harmonized across all green benchmarks.

*Table S5: Green hydrogen benchmark.*

| Target co-product | Process description | LCI with activities from ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|---|
| 1 kg of green hydrogen | Wind-powered water electrolysis, Vasquez et al. [9] | electricity production, wind, 1-3MW turbine, onshore | RoW | kWh | 64.1 |
| | | water production, ultrapure | RoW | kg | 11 |

*Table S6: Green CCU-based formic acid benchmark.*

| Target co-product | Process description | LCI with activities from ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|---|
| 11.4 kg of formic acid | Vasquez et al. [9]: Wind-powered water electrolysis | Hydrogen (Table S5) | RoW | kg | 0.81 |
| | Sternberg et al. [10]: carbon capture and utilization with direct air capture | electricity production, wind, 1-3MW turbine, onshore | RoW | kWh | 5.5 |
| | | heat production, wood chips from industry, at furnace 300kW | RoW | MJ | 134.2 |
| | | Carbon dioxide, fossil (air) | Biosphere | kg | 10.9 |

*Table S7: Green bio-methanol-based acetic acid benchmark.*

| Target co-product | Process description | LCI with activities from ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|---|
| 14.9 kg of acetic acid | Adapted calanese process in ecoinvent (based on Monsanto process): methanol from wood chips | acetic acid, without water, in 98% solution state | GLO | kg | 14.9 |
| | Fossil methanol replacement | market for methanol, from biomass | RoW | kg | 8.0 |
| | Fossil electricity replacement | electricity production, wind, 1-3MW turbine, onshore | RoW | kWh | 0.85 |
| | Fossil heat replacement | heat production, wood chips from industry, at furnace 300kW | RoW | MJ | 20.9 |

*Table S8: Green glucose-based lactic acid benchmark.*

| Target co-product | Process description | LCI with activities from ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|---|
| 22.4 kg of lactic acid | Winter et al. [7] (based on [11]): "To produce PLA, glucose is fermented into lactic acid, followed by an array of downstream monomer separation and purification processes. " | market for glucose | GLO | kg | 28.8 |
| | | market for tap water | RoW | kg | 0.49 |
| | | market for calcium carbonate, precipitated | RoW | kg | 18.9 |
| | | market for methanol, from biomass | RoW | kg | 0.02 |
| | | market for sulfuric acid | RoW | kg | 30.2 |
| | | electricity production, wind, 1-3MW turbine, onshore | RoW | kWh | 29.3 |

*Table S9: Green glucose-based succinic acid benchmark.*

| Target co-product | Process description | LCI with activities from ecoinvent version 3.9 | Location | Unit | Amount |
|---|---|---|---|---|---|
| 1 kg of succinic acid | Winter et al. [7] (based on [12]):<br><br>Anaerobic fermentation | market for glucose | GLO | kg | 21.9 |
| | | market for tap water | RoW | kg | 455.7 |
| | | carbon dioxide production, liquid | RoW | kg | 4.2 |
| | | market for sodium | GLO | kg | 1.9 |
| | | heat production, wood chips from industry, at furnace 300kW | RoW | MJ | 142.1 |
| | | electricity production, wind, 1-3MW turbine, onshore | RoW | kWh | 32.5 |

# S4 Economic potential

We introduce the economic potential to calculate the margin of expected revenues from hydrogen and the co-produced acid and the expected costs of each dehydrogenation route with complete feedstock conversion. We neglect investment costs for plant construction and energy demands for the operation since some routes are early-stage technologies for which the data is unavailable. For each dehydrogenation route j, only bio-alcohol feedstock costs are included and calculated with market prices $c_j$. We assume that water is free of charge. Therefore, the total costs of a dehydrogenation route $j$ are equal to the feedstock costs $C_j$ from bio-alcohol feedstock. Multiplying the feedstock market prices $c_j$ with the feedstock mass $m_j$ per functional unit provides the costs $C_j$ in the dehydrogenation route $j$.

$$C_j = m_j \cdot c_j \tag{S1}$$

We assume that the dehydrogenation route's product selling prices are equal to the benchmarks' selling prices to be competitive. Furthermore, we assume that the benchmarks' product selling prices are represented by market prices. We calculate the expected revenues R with the market prices of hydrogen $c_{hydrogen}$ and co-produced acid $c_{,acid}$ and the mass m in the functional unit.

$$R_j = R_{acid,j} + R_{hydrogen} = m_{acid,stoichiometric,j} \cdot c_{acid,j} + m_{hydrogen} \cdot c_{hydrogen} \tag{S2}$$

Next, we include carbon taxes. We calculate the carbon tax benefit of the dehydrogenation route $j$ by (i) including carbon taxes of the dehydrogenation route to the production costs and (ii) including carbon taxes of the benchmark technologies. The carbon tax $C_{carbon\ tax}$ is the product of the global warming impact in $EI_{climate\ change}$ and the carbon price $c_{carbon\ EU-ETS}$.

$$C_{carbon\ tax} = EI_{climate\ change} \cdot c_{carbon\ EU-ETS} \tag{S3}$$

The carbon tax advantage $C_{\text{carbon tax advanatage}}$ of the dehydrogenation route $j$ is the difference of the carbon emission tax of the dehydrogenation route and the benchmark.

$$R_{\text{carbon tax advanatage},j} = C_{\text{carbon tax,benchmark},j} - C_{\text{carbon tax,dehydrogenation route},j} \quad \text{(S4)}$$

The economic potential $E_{\text{pot,econ},i}$ includes revenues, the carbon tax advantage, and the costs and is calculated as:

$$E_{\text{pot,econ},j} = R_{\text{acid},j} + R_{\text{hydrogen}} + R_{\text{carbon tax advantage},j} - C_{\text{alcohol feedstock},j} \quad \text{(S5)}$$

Overall, the resulting profit margin that we call the economic potential (Equation S5) is an optimistic margin since additional costs must be included in the industrial scale which decreases the environmental potential. For example, additional costs arise from the dehydrogenation plant construction, and additional utilities, such as downstream product separation. However, a higher carbon tax increases the economic potential.

The chemical prices in Table S10 are used to calculate the economic potentials of the dehydrogenation routes, which are taken from global trading platforms.

*Table S10: Prices of chemicals and carbon emissions.*

| Chemicals | Price in USD/kg | Reference |
|---|---|---|
| Feedstocks | | |
| ethanol | 1 | [13] |
| propanediol | 1.25 | [13] |
| butanediol | 1.16 | [14] |
| methanol | 0.38 | [15] |
| Tap water | Assumed to be free of charge | |
| Products | | |
| hydrogen | 1 | [13] |
| acetic acid | 0.43 | [16] |
| formic acid | 0.68 | [13] |
| lactic acid | 1.9 | [13] |
| succinic acid | 2.05 | [13] |
| adipic acid | 1.7 | [13] |
| Carbon tax | | |
| EU-ETS carbon price | 0.11 USD/kg $CO_2$ | [17] |

| Exchange rate | 1.08 €/$ | | [18] |
|---|---|---|---|
| Heat | | | |
| Natural gas | 1.91 USD/MMBtu | | [19] |

# S5 Extended methods

In the main manuscript, the feedstock contributions in the fossil benchmarks are presented to discuss the environmental potential. We argue that the remaining contributions can be caused by, e.g., heat demands. The environmental potential is therefore turned into lower reaction yield and allowed heat demand to investigate more realistic dehydrogenation processes. In Section S4.1 we present the assessment of feedstock contributions. In Section S4.1 we present the reaction yield and heat demand calculations, and in Section S4.3 we present the incineration model that is used to account for unreacted feedstock in reaction yields below 100%.

## S5.1 Aggregated feedstock contributions in fossil benchmarks

We calculate the feedstock contribution in the fossil production of acids and hydrogen based on the contribution analysis in the Activity Browser [20]. In the Activity Browser, the cut-off level in the contribution analysis sets a threshold so that all activity contributions with a contribution below the threshold are neglected. The lowest applicable impact cut-off in the activity browser corresponds to 0.001 % and was used to collect and aggregate contributions from feedstock activities in the LCI of the foreground systems of the fossil benchmark products from the Sankey diagrams. Hereby, contributions from the single feedstocks were separated from the rest and aggregated to the total feedstock contributions. We distinguish between feedstock contributions and a rest that covers other contributions, e.g., energy demands and infrastructure (Figure S1).
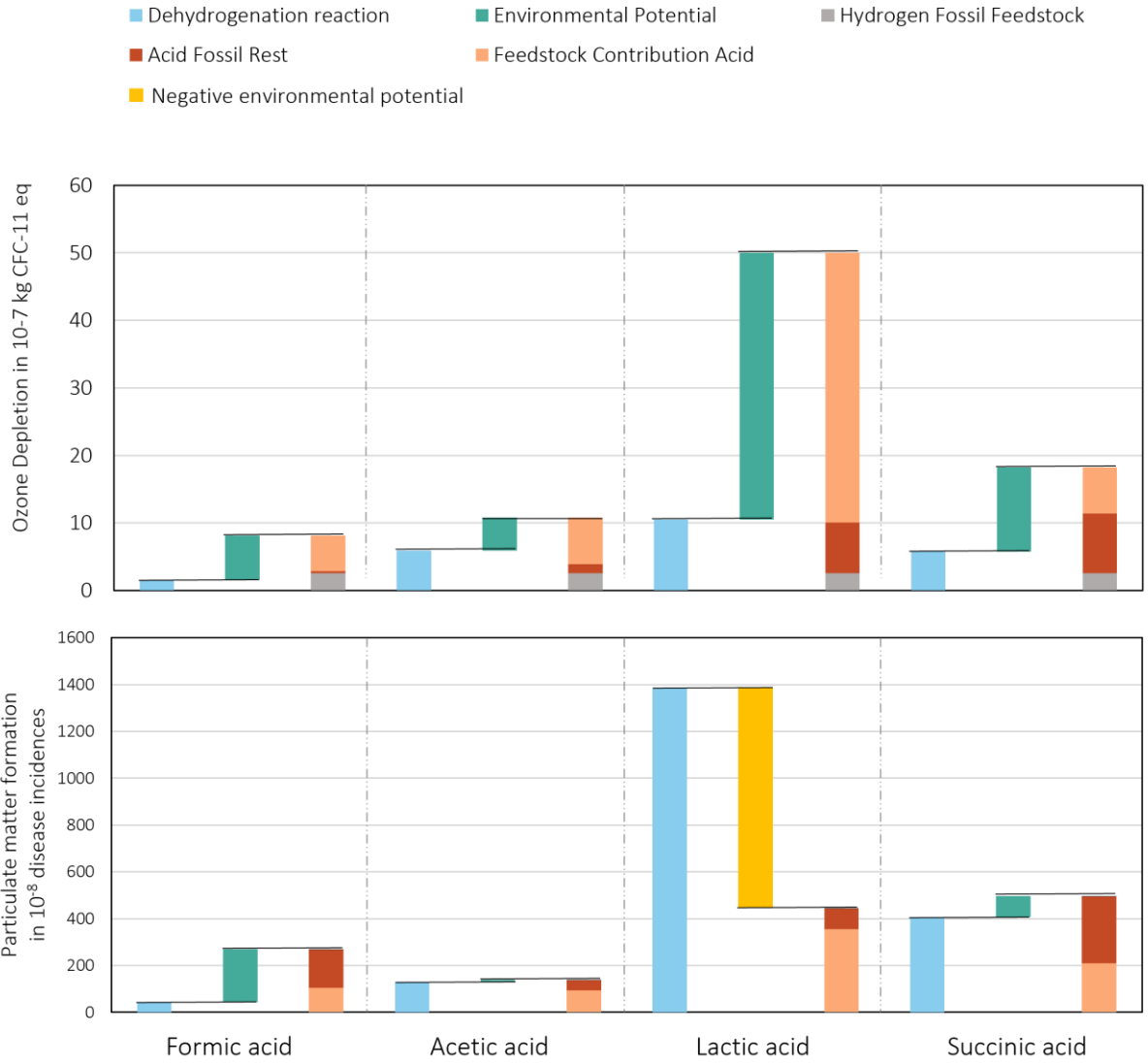
*Figure S1: Environmental potentials and contributions of dehydrogenation routes and benchmarks in ozone depletion and particulate matter formation.*

## S5.2 Minimum reaction yield and allowed heat demand

A positive environmental potential allows for a decrease in reaction yield, here resulting in increased feedstock demand up to the minimum reaction yield that is reached when the environmental potential turns zero (i.e., the environmental impact of the dehydrogenation route and the benchmark are equal). We introduce the reaction yield $\gamma$ and calculate the excess feedstock in Equation S6 that arises with incomplete feedstock conversion for a reaction yield $\gamma$ below 1, where 1 corresponds to complete feedstock conversion. The feedstock mass $m_{\text{feedstock,FU}}$ in the functional unit is constant. Consequently, the excess feedstock mass is zero when the reaction reaches complete feedstock conversion.

$$m_{\text{feedstock,excess}} = \frac{1}{\gamma} \cdot m_{\text{feedstock,FU}} - m_{\text{feedstock,FU}} = \left(\frac{1-\gamma}{\gamma}\right) \cdot m_{\text{feedstock,FU,}}$$

(S6)

$$\text{where } \gamma = \frac{m_{\text{feedstock,FU}}}{m_{\text{feedstock,available}}} = \frac{m_{\text{feedstock,FU}}}{m_{\text{feedstock,FU}} + m_{\text{feedstock,excess}}}$$

The excess feedstock needs to be classified as a product or waste and treated accordingly in the LCA. For consistency, we incinerate the excess feedstock in each dehydrogenation route $j$. We calculate the incineration impacts $\text{EI}_{\text{incineration alcohol}}$ with the Doka model [21] based on the atomic composition of the feedstock bio-alcohols (more information in Section S5.3) so we can add the incineration impacts to the global warming impact in the climate change impact category.

Next, we calculate the incineration impacts $\text{EI}_{\text{incineration feedstock},j}$ of each dehydrogenation route $j$ by multiplication of the excess feedstock mass and the alcohol's incineration impact.

$$\text{EI}_{\text{incineration feedstock},j} = m_{\text{feedstock,excess}} \cdot \text{EI}_{\text{incineration alcohol},j}$$

$$= \left(\frac{1-\gamma}{\gamma}\right) \cdot m_{\text{feedstock,FU}} \cdot \text{EI}_{\text{incineration alcohol},j}$$

(S7)

A positive environmental potential can also be translated into heat demands, e.g., from natural gas boilers. The allowed heat demand is, therefore, multiplied by the environmental impact of natural gas production (market for heat, district or industrial, natural gas, RoW) from ecoinvent. We include the reaction yield $\gamma$ and the allowed heat demand $Q_{\text{allowed heat demand}}$ in the

environmental potential equation to calculate the trade-off between decreasing reaction yield and additional natural gas demand. The fossil benchmark impacts $\text{EI}_{j,\text{benchmark}}$ remain constant. In Equation S8, the environmental potential $\text{E}_{\text{pot,econ},j}$ is set to zero which represents equal environmental impacts of the benchmark and the dehydrogenation route. In other words, dehydrogenation represents a technology as sustainable as the benchmark.

$$\text{E}_{\text{pot,env},j} = \text{EI}_{\text{benchmark},j} - \frac{1}{\gamma} \cdot \text{EI}_{\text{dehydrogenation},j} - \left(\frac{1-\gamma}{\gamma}\right) \cdot \text{EI}_{\text{incineration feedstock},j}$$
$$- Q_{\text{allowed heat demand}} \cdot \text{EI}_{\text{heat,natural gas}} = 0$$

(S8)

Now, Equation S8 can be rearranged, so that the allowed heat demand $Q_{\text{allowed heat demand}}$ depends on the reaction yield $\gamma$ (Equation S4).

$$Q_{\text{allowed heat demand}} \cdot \text{EI}_{\text{heat,natural gas}} =$$

$$\text{EI}_{\text{benchmark},j} - \frac{1}{\gamma} \cdot \text{EI}_{\text{dehydrogenation},j} - \left(\frac{1-\gamma}{\gamma}\right) \cdot \text{EI}_{\text{incineration feedstock},j}$$

(S9)

The minimum reaction yield $\gamma_{\text{min}}$ is reached when the allowed heat demand $Q_{\text{allowed heat demand}}$ is zero and, the maximum allowed heat demand $Q_{\text{allowed heat demand,max}}$ is reached when the reaction yield $\gamma$ is 1.

## S5.3 Incineration model

We assume the excess feedstock arising from a reaction yield below 100% is incinerated. A particularity arises in the Environmental Footprint EN15804 Cut-off method that accounts for biogenic carbon uptake as negative climate change impacts [22]. Here, biomass growth can result in a negative global warming impact. In the cut-off approach, wastes from a process are provided to subsequent processes burden-free, and all environmental impacts are allocated to the products of the original process using the biomass. In the sugarcane-based ethanol production in the ecoinvent database, a relevant mass of burden-free vinasse waste arises. In the cut-off approach, the total sugarcane carbon uptake is allocated to ethanol production. At the end of life, the incineration of ethanol results in lower carbon emissions than the total allocated carbon uptake to the ethanol product. As a result, the incineration of ethanol leads to

net-negative emissions. To balance the carbon uptake and emission, we incinerate sugarcane that is based on sucrose molecules instead of ethanol.

In the other dehydrogenation routes, no burden-free biomass waste is being produced and used in subsequent processes other than waste treatment as far as we can trace back via background activities in the database.

## S6 Extended results

We calculated the environmental potentials in all impact categories of the Environmental Footprint EN15804 Cut-Off method. The most important results in impact categories of quality level I and II are presented in the main manuscript (Section 3.1-3.2). Further results are discussed in the following sections S6.1 for quality levels I and II and S6.2 for quality levels II/III and III.

### S6.1 Extended results: environmental potential in impact category quality levels I and II

In the fossil benchmark scenario, the environmental potential in ozone depletion is nine to twelve orders of magnitude lower than the ozone depletion impact of harmful halocarbons [23], and, therefore, negligible. The negative environmental potential of the lactic acid route arises with the large heat amount of propanediol feedstock production. The heat is supplied by wood chip incineration, which leads to high impacts in particulate matter formation leading to a negative environmental potential of $-940^{-8}$ disease incidences.

In the green benchmark scenario, the dehydrogenation to succinic acid performs better than the benchmark and achieves positive environmental potentials in the eutrophication impact categories with a crop-based feedstock because the benchmark feedstock is identical. The contribution analysis of the individual impact categories indicates that the feedstock and energy demands are crucial when the bio-feedstock and energy supply in the dehydrogenation route and the benchmark are identical. For example, propanediol feedstock for dehydrogenation to lactic acid and the benchmark feedstock are glucose-based. However, propanediol production consumes 25 % more glucose and substantial heat from burning wood chips, while the

benchmark consumes more wind electricity. The environmental impacts associated with the higher glucose consumption and heat from wood chips exceed the benchmark. As a consequence, dehydrogenation to lactic acid performs poorly in various impact categories. The butanediol feedstock for dehydrogenation to succinic acid and the benchmark feedstock are also glucose-based with similar life cycle inventories, but the succinic acid benchmark requires three times more heat and consumes energy-intensive liquid $CO_2$ and sodium. Thereby, the dehydrogenation to succinic acid achieves promising environmental potentials.

For all four dehydrogenation routes, we observe an increase in environmental potential in particulate matter formation. Particulate matter formation is associated with the combustion of coal and biomass [24], as observed in the case study for heat supply from burnt wood, and harvesting and fertilizer use in agriculture [25]. The increase of environmental potential in particulate matter formation in the green benchmark scenario is, thus, a consequence of the heat supply from wood chips incineration in the green benchmarks.

## S6.2 Extended results: environmental potential in impact category quality levels II/III and III

The results in impact categories of quality level II/III and III are summarized in Tables S11 and S12. In addition to the impact categories discussed in the main manuscript, the dehydrogenation to formic acid results in more positive environmental potentials than the other dehydrogenation routes in the fossil benchmark scenario (Table S11); more precisely, all environmental potentials are positive except for land use. Overall, the biomass growth for feedstocks in the dehydrogenation routes leads to negative environmental potentials in land use in all dehydrogenation routes in the fossil benchmark scenario. Furthermore, agricultural crop growth for feedstocks in acetic acid, lactic acid, and succinic acid from dehydrogenation leads to negative environmental potentials in water use. The fertilizer use associated with agricultural crop growth leads to negative environmental potentials in freshwater ecotoxicity and non-

carcinogenic human toxicity. The use of methanol from wood chips for dehydrogenation to formic acid leads to a negative environmental potential in land use.

In the green benchmark scenario, the dehydrogenation to succinic acid results in positive environmental potentials in all impact categories in quality levels II/III and III. In the green benchmark scenario, biomass-based dehydrogenation is compared to biomass-based acid benchmark processes, except for formic acid from carbon capture and utilization. Therefore, the environmental potential depends on feedstock amounts and benchmark energy demands. The large heat consumption in the succinic acid benchmark leads to environmental impacts that exceed the dehydrogenation route impacts leading to a positive environmental potential in all impact categories in Table S12 in the succinic acid dehydrogenation route.

*Table S11: Environmental potentials of dehydrogenation to hydrogen and four co-products in a fossil benchmark scenario in the impact categories of quality levels II/III and III. The green intensity increases with positive potential in comparison to the co-product options within the same impact category and benchmark scenario. Negative potentials are displayed in orange.*

| Fully fossil benchmark scenario | | | | | | | |
|---|---|---|---|---|---|---|---|
| Dehydrogenation to hydrogen and co-products | Order of magnitude | | | | | | |
| | $10^{-9}$ | $10^{-8}$ | $10^2$ | $10^3$ | $10^2$ | $10^{-5}$ | $10^1$ |
| Impact Categories | Human Toxicity: Carcinogenic in CTUh | Human Toxicity: Non-Carcinogenic in CTUh | Ecotoxicity: Freshwater in CTUe | Energy Resources: Non-Renewable in MJ, net calorific value | Land Use in dimensionless | Material Resources: Metals/Minerals in kg SB eq | Water Use in m3 world eq deprived |
| Quality Level | II/III | | | III | | | |
| Formic Acid | 10 | 28 | 2 | 8 | -20 | 14 | 7 |
| Acetic Acid | -71 | -96 | -21 | 8 | -9 | 13 | -4 |
| Lactic Acid | 1 | -26 | -8 | 10 | -18 | 10 | -16 |
| Succinic Acid[3] | 76 | -6 | -7 | 10 | -5 | -10 | -9 |

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[3] Succinic acid replaces adipic acid in the fossil benchmark scenario.

Table S12: Environmental potentials of dehydrogenation to hydrogen and four co-products in a green benchmark scenario in the impact categories of quality levels II/III and III. The green intensity increases with positive potential in comparison to the co-product options within the same impact category and benchmark scenario. Negative potentials are displayed in orange.

| Fully green benchmark scenario | | | | | | | |
|---|---|---|---|---|---|---|---|
| Dehydrogenation to hydrogen and co-products | Order of magnitude | | | | | | |
| | $10^{-9}$ | $10^{-8}$ | $10^{1}$ | $10^{1}$ | $10^{2}$ | $10^{-5}$ | $10^{-1}$ |
| Impact Categories | Human Toxicity: Carcinogenic in CTUh | Human Toxicity: Non-Carcinogenic in CTUh | Ecotoxicity: Freshwater in CTUe | Energy Resources: Non-Renewable in MJ, net calorific value | Land Use in dimensionless | Material Resources: Metals/Minerals in kg SB eq | Water Use in m3 world eq deprived |
| Quality Level | II/III | | | III | | | |
| Formic Acid | 11 | -2 | -2 | -2 | -17 | 2 | -5 |
| Acetic Acid | -59 | -77 | -208 | 47 | 14 | 18 | -380 |
| Lactic Acid | 12 | 147 | -8 | -19 | -11 | 198 | -398 |
| Succinic Acid | 18 | 26 | 1 | 7 | 3 | 7 | 2 |

## S6.3 Extended results: impact contributions of fossil feedstock in dehydrogenation routes

In the fossil benchmark scenario, the impact contribution from fossil hydrogen production remains below 30% in the dehydrogenation benchmarks and 20% in all the impact categories in the main manuscript and SI. In the green benchmark scenario, the contribution of green hydrogen production from water electrolysis is equal to or below 10% in the lactic acid, and succinic acid dehydrogenation benchmarks, below 17% in the acetic acid dehydrogenation benchmark, and below 45% in the formic acid dehydrogenation benchmark for all impact categories. The highest contributions from hydrogen production in the formic acid dehydrogenation benchmark occur in ecotoxicity, ozone depletion, and material resources and are associated with the wind turbine construction for wind electricity and seawater osmosis for ultrapure water production. In these

impact categories, the environmental impact per kg of product exceeds the formic acid production. The main contribution in formic acid production from carbon capture and utilization comes from wood chip incineration for heat supply to cover the large heat demand; the relative feedstock contribution is minor compared to other dehydrogenation acid benchmarks. Nonetheless, the formic acid amount exceeds the hydrogen amount by a factor of 11. Consequently, the relative environmental impact contribution from hydrogen production increases.

## S6.4 Extended results: sensitivity analysis on economic potential

We study the trade-off between reaction yield (related to feedstock costs) and heat demand (related to energy costs) (for, e.g., thermochemical reaction and separation) to calculate economic performance targets.

The economic potential is, in general, already positive for lower reaction yields (below 10 %) than the environmental potential. This finding holds for lactic acid, formic acid, and succinic acid (Fig. S.2). Assuming industrial-scale reaction yields, a margin of 18860 MJ natural gas remains for succinic acid, 15840 MJ for lactic acid, 6337 MJ for formic acid, and 580 MJ for acetic acid. The remaining margins are higher than the heat demands of the industrial benchmarks and reaction enthalpies (see Section S.2). For acetic acid, the economic potential is the limiting factor. Here, the economic potential increases the minimum reaction yield to 46% from 19% with the environmental potential (Section 4.2).
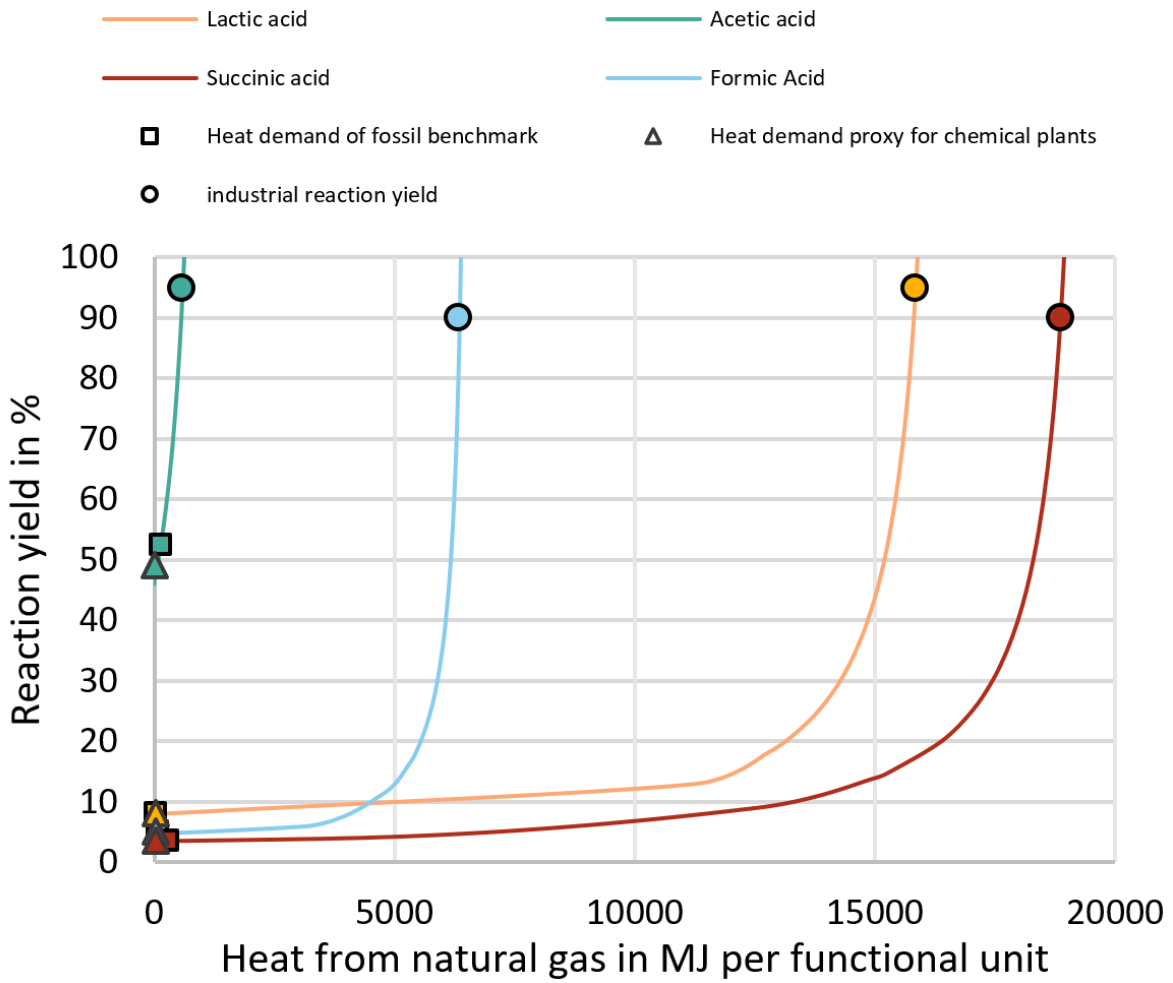
*Figure S.2: Trade-off for dehydrogenation routes between reaction yield and allowed heat demand to arrive at zero economic potential for the fossil benchmark scenario. A lower reaction yield implies higher feedstock costs. An increasing heat demand implies higher natural gas costs. Feedstock prices and the natural gas price are taken from Table S10. The economic potential is presented in the main manuscript Fig. 4. The triangles represent heat demands based on a proxy for chemical plants 57. The squares represent the heat demands of the fossil benchmarks. The circles represent industrial reaction yields.*

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