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Future opportunities

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Life cycle assessment of hexanoic acid production via microbial electrosynthesis and renewable electricity: Future opportunities

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ABSTRACT

Microbial electrosynthesis (MES) is a novel carbon utilisation technology aiming to contribute to a circular economy by converting CO₂ and renewable electricity into value-added chemicals. This study presents a cradle-to-gate life cycle assessment (LCA) of hexanoic acid (C6A) production using MES, comparing this production with alternative technologies. It also includes a cradle-to-grave LCA for potentially converting C6A into a neat sustainable aviation fuel (SAF). On a cradle-to-gate basis, MES-based C6A exhibits a carbon footprint at 5.5 t CO₂eq/tC6A, similar to fermentation- and plant-based C6A. However, its direct land use is more than one order of magnitude lower than plant-based C6A. On a cradle-to-grave basis, MES-based neat SAF emits 325 g CO₂eq/MJ neat SAF, which is significantly higher than the counterparts from currently certified routes and conventional petroleum-derived jet fuel. However, its negligible indirect land use change emissions might potentially make it competitive against neat SAFs originating from first-generation biomass.

1. Introduction

Direct electrochemical conversion of CO₂ to chemicals powered by renewable electricity can play a key role in the energy transition in the chemical sector. Some studies have investigated the environmental impacts of small-molecule products, which are usually commodity chemicals with a low market price, such as chlorine [1], methane, ethanol, and ethylene [2]. Insight into the potential for converting CO₂ to larger molecules is currently limited. In recent years, the conversion of CO₂ to carboxylic acids (e.g., propionic acid, butyric acid, valeric acid, and hexanoic acid [3]) with a longer carbon chain via microbial electrosynthesis (MES) has caught the attention of researchers [4,5]. These chemicals do not only have a higher economic value as compared to shorter C-chain chemicals but can also be used as a platform chemical and for synthesising fuels [6,7]. Among the carboxylic acids that MES can produce, hexanoic acid (C6A), also known as caproic acid, has the highest market price between 2.5 and 4.2 €/kg [8] and is used, among others, as a food additive, precursor to lubricants, and antimicrobial in pharmaceuticals [9]. Therefore, some researchers are particularly interested in producing C6A from CO₂ via either MES [8] or bio-fermentation [10]. Production of C6A from CO₂ through MES has three

key advantages:

- I. MES can be driven by renewable electricity and converts CO₂ into a valuable product, thereby fitting with the need to defossilise chemical production [11,12].
- II. C6A can be catalytically upgraded to *n*-alkanes via ketonisation and subsequent hydrodeoxygenation [13,14]. On average, *n*-alkanes make up about 20 wt% of current Jet A fuel [15,16]. Synthetic *n*-alkanes can be potentially blended with petroleum-derived jet fuel to a maximum of 50 vol% [15,17], denoted as neat sustainable aviation fuel (SAF) [18] or neat synthetic kerosene [19]. SAFs are an essential option for defossilising jet fuels, with a market size estimated at 230 billion gallons (equivalent to 870 million m³) in 2050 [15,20]. The ideal carbon chain length for aviation fuels is between 8 and 16 [15, 21], with an average carbon number of 11.4 [13,14]. The ketonisation has experimentally converted 98 wt% of C6A to C₈-C₁₆ *n*-alkanes [14], with an average carbon chain length of 11 [14] or 11.3 [13]. These characteristics could potentially qualify *n*-alkanes from C6A as a neat SAF. Adoption of the ketonisation route for neat SAF would, however, require a massive increase in C6A

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production. As a reference, C6A is projected to reach a global market of ca. 100 kt/y in 2027 [22] (see [supplementary materials](#) for details).

III. The current commercial production method of C6A is the fractional distillation of coconut or palm kernel oil [9] where C6A is a by-product accounting for less than 1 wt% of the products. Hence, it is subject to limited resources [6] (e.g., exporting bans on plant oils as recently happened in Indonesia) and sustainability concerns [23].

The sustainability of hexanoic acid will play an important role in its further use in new markets. In previous work, we designed a process model for MES-based C6A in Aspen Plus and assessed its techno-economic performance integrated with an intermittent source of electricity [24].

To date, there is limited information on the potential environmental impact of C6A production via MES. Sadhukhan [3] evaluated the global warming potential of the production of a range of carboxylic acids (incl. C6A) at an equipment level, the results of which are directly visualised at <https://tesarrec.web.app/sustainability/mes>. In [25], the authors carried out a carbon footprint of C6A from fermentation at a plant level, however, within a gate-to-gate scope. This paper aims to provide a better understanding of the environmental footprint of producing C6A via MES to supply the current market and as a potential feedstock for neat SAF.

2. Methodology

To identify and assess the potential environmental impacts, a life cycle assessment (LCA) was conducted, assuming two future deployment scenarios for C6A. The details are further explained in this section.

2.1. Production of hexanoic acid

Fig. 1 gives an overview of the production of C6A via MES. In the anode chamber of the MES reactor, water is converted into H^+ and O_2 . O_2 leaves the reactor via the headspace, while H^+ permeates the membrane to reach the cathode chamber. In there, CO_2 is fed as a carbon source while $Ca(OH)_2$ is dosed to control the pH. Microbial cells that

grow on the cathode convert the CO_2 with electrons and H^+ to produce aqueous hexanoate via acetate and butyrate. After the MES unit, the hexanoate is acidified to C6A by H_3PO_4 . Next, C6A is recovered by liquid-liquid extractions using trioctylamine (TOA), followed by solvent regeneration. Finally, the stream is dehydrated to reach the market purity requirement of 99 wt%.

In this paper, we depart from a process model of C6A production via MES developed in previous work [24]. A nominal capacity of 10 kt/y of purified C6A was assumed. According to the reaction stoichiometry, O_2 was produced as a by-product at about 22 kt/y, and it was compressed to 80 bar. The plant was designed for continuous operation (8760 h/y). It is assumed to be situated in the Port of Rotterdam (the Netherlands) and powered by renewable electricity from dedicated wind and solar farms nearby (see [supplementary materials](#) for additional information). To reduce the impact of fluctuations, a storage tank (ST) was used as a buffer. The ST was placed before the first solvent regeneration column (see Fig. 1). The tank's size and the scheduling of the entire plant were optimised to reach a maximum annualised net profit under the pre-selected hybrid renewable electricity profile on an hourly basis. This resulted in an ST size of 35 m^3 , which allows to produce ca. 8 kt of C6A per year [26]. Specifications of the MES reactor and heat and mass balances of the plant are summarised in the [supplementary materials](#).

Two scenarios were studied to understand the potential environmental impacts of MES-based C6A:

- Scenario I: MES-C6A would fulfil the market demand of *current* applications
- Scenario II: MES-C6A would be used to produce neat SAF, which is a potential *new* application.

2.2. Life cycle assessment

An ex-ante LCA was performed for a hypothetical N^{th} -of-a-kind plant, following ISO 14044 [27]. We used SimaPro 9.6 and the databases Ecoinvent 3.8 [28] and Agri-footprint 5.0 [29]. The method selected for the life cycle impact assessment (LCIA) was ReCiPe Midpoint H. The environmental impacts from infrastructure were not included in this study as their contribution is expected to be marginal [30].

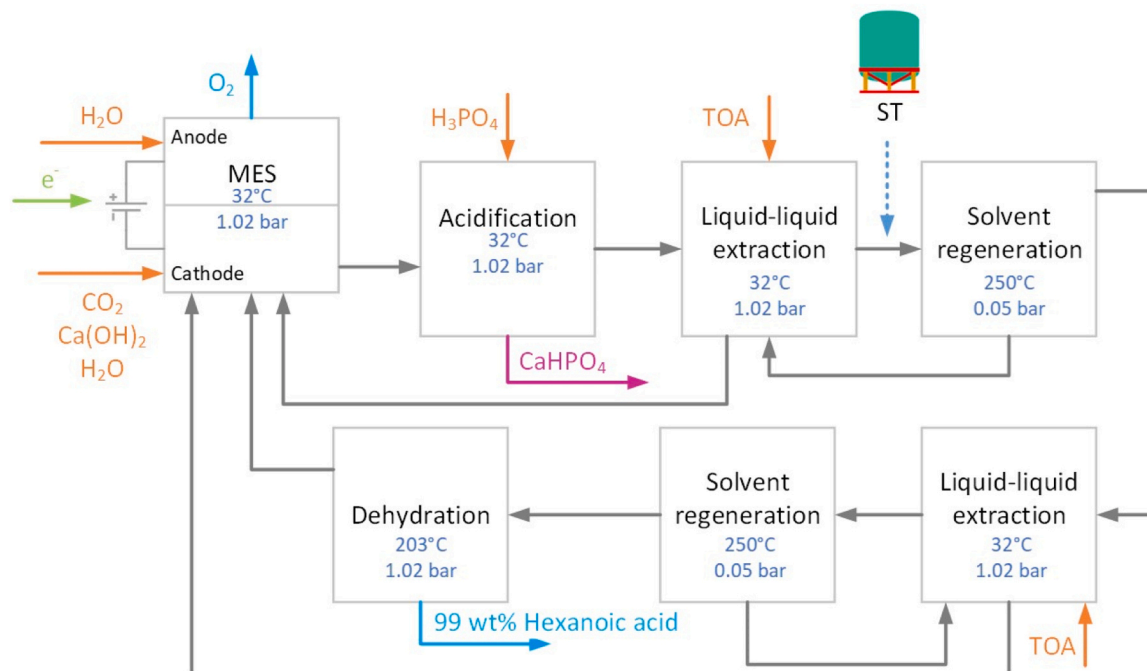


Fig. 1. Simplified block flow diagram of producing hexanoic acid via microbial electrosynthesis (MES). ST: storage tank. TOA: trioctylamine.

As indicated in Fig. 1, the plant produces both hexanoic acid and oxygen, with the amount of oxygen being twice that of hexanoic acid. The multifunctionality due to O₂ co-production was treated in two ways: 1) economic allocation and 2) system expansion with substitution in the manner of subtraction (referred to as substitution hereafter).

2.2.1. Scenario I

2.2.1.1. System boundary. In this scenario, the MES-based C6A would displace the counterfactual C6A, and it is assumed to have the same product functionality (same chemical composition), the system boundary was set as cradle-to-gate. The foreground system focuses on the activities that are specific to this study and includes CO₂ capture (solvent used: monoethanolamine), CO₂ transport, and C6A production, as shown in Fig. 2. The source of CO₂ is assumed to be the flue gas of a point source. The flue gas is therefore considered a waste stream, and therefore, following ISO guidelines, 100 % of resources and emissions are allocated to the products of the point source [31]. This implies that the emissions allocated to the systems are only those of the CO₂ capture unit. The background system includes heat, chilling, and electricity generation, solvents and other chemicals production, and transportation, as outlined in Fig. 2.

2.2.1.2. Functional unit and indicators. The selected functional unit was one tonne of produced C6A. In this scenario, three impact categories are addressed. Since MES is a carbon utilisation technology, global warming potential (GWP; t CO₂eq/t C6A) was selected as the first indicator. The second indicator was land use change (LUC; m²a crop eq/t C6A) because it is a key bottleneck for the current production pathway, and the MES plant requires dedicated solar and wind farms, which can require a significant amount of land for their installation. LUC can be decomposed into direct land use change (dLUC) and indirect land use change (iLUC). dLUC occurs when cropland is converted for production or service [32]. iLUC happens when changes in the use of existing cropland for production or service would result in those goods or services (e.g., food) being produced on another (crop)land [33]. Although iLUC emissions (t CO₂eq/t C6A) are important, there is a lack of data due to the challenges in quantification. Hence, they are not incorporated into the GWP calculation in SimaPro but are discussed separately in this study. Direct land occupation decoupled from the time factor (DLO; m²) was estimated for the renewable electricity farms and the MES plant based on their capacities. Finally, water consumption (m³/t C6A) was included as it is a key reactant for the MES and is also used as a cooling utility (i.e., make-up cooling water), and it is a key concern for plant-based C6A production. Water consumption refers to “freshwater withdrawals which are evaporated, incorporated into products and waste, transferred to different watersheds, or disposed into the land or sea after usage” [34].

2.2.1.3. Reference system and comparison to other studies. For the reference system, a coconut oil production route was selected. The system boundary is depicted in Fig. 3. In the foreground system are crude coconut oil (CCO) production, CCO transport, and C6A production. The CCO was assumed to be imported from Southeast Asia to Europe to produce C6A. Data obtained from Ecoinvent was used for these activities. As C6A is a by-product in the CCO route (accounting for less than 1 wt%), the emissions were allocated between C6A and other fatty acids using economic allocation.

As mentioned in Section 2.1, the MES system also produces oxygen as a by-product. In the reference system, it was assumed that O₂ is produced using an air separation unit (ASU). The data was obtained from Ecoinvent and was used for substitution.

Finally, for comparison purposes, GWP data for fermentation-based hexanoic acid produced from waste, an alternative production route, was gathered from [25] and the DLO of the pilot plant based on this fermentation route was used for discussion (<http://www.chaincraft.nl/>).

2.2.1.4. Life cycle inventory. Life cycle inventories (LCI) of the MES and coconut routes are provided in Appendix A. For the MES route, except for the electricity used to directly power the MES plant (scope 1), emissions from other utilities were accounted for in scope 2 and based on natural gas. The electricity used to regenerate cooling water belonged to scope 2 utility and was also assumed to have originated from natural gas. From here onward, electricity refers to scope 1 electricity; utility refers to scope 2 utility. For the reference (coconut route), utilities (scope 2) were from a mix of fossil and non-fossil fuels, as reported in Ecoinvent. Although it can be expected that in the future, the background systems will entirely rely on renewable sources, we decided to keep the background system as of today to better explore the impact of changes in the foreground versus the background system.

Regarding solvents (i.e., monoethanolamine and TOA) and other chemicals (i.e., Ca(OH)₂ and H₃PO₄), since TOA and Ca(OH)₂ were not available in Ecoinvent, analogous compounds (i.e., triethylamine and Al(OH)₃, respectively) were used in the LCI.

2.2.1.5. Sensitivity analysis. To assess the impacts of changes in the background system, for the MES route, the impact of the carbon footprint from utilities on the GWP per functional unit was assessed via one-at-a-time sensitivity analyses.

In addition, since coconut is used in the reference system, we compared the relevant data in two different databases: Ecoinvent 3.8 and Agri-footprint 5.0. We could not directly compare the environmental metrics for hexanoic acid between these two databases owing to the lack of any fatty acid data in Agri-footprint. Thus, we used the impacts allocated to CCO production for comparison and analysed between both databases.

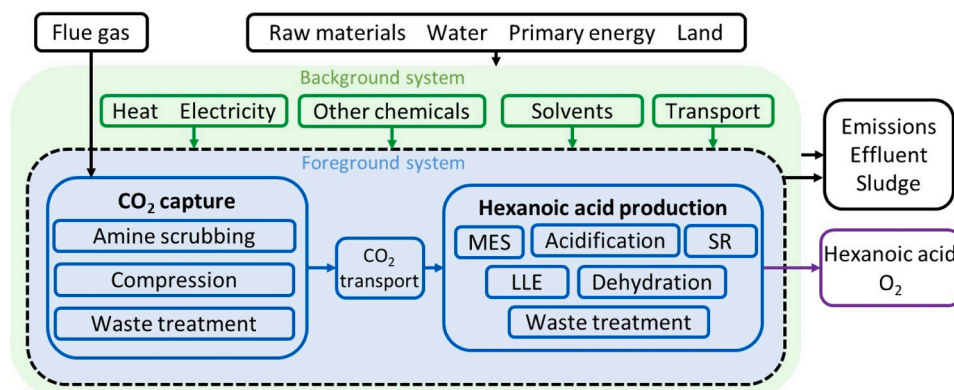


Fig. 2. System boundary of MES-based hexanoic acid in Scenario I. MES: microbial electrosynthesis. SR: solvent generation. LLE: liquid-liquid extraction.

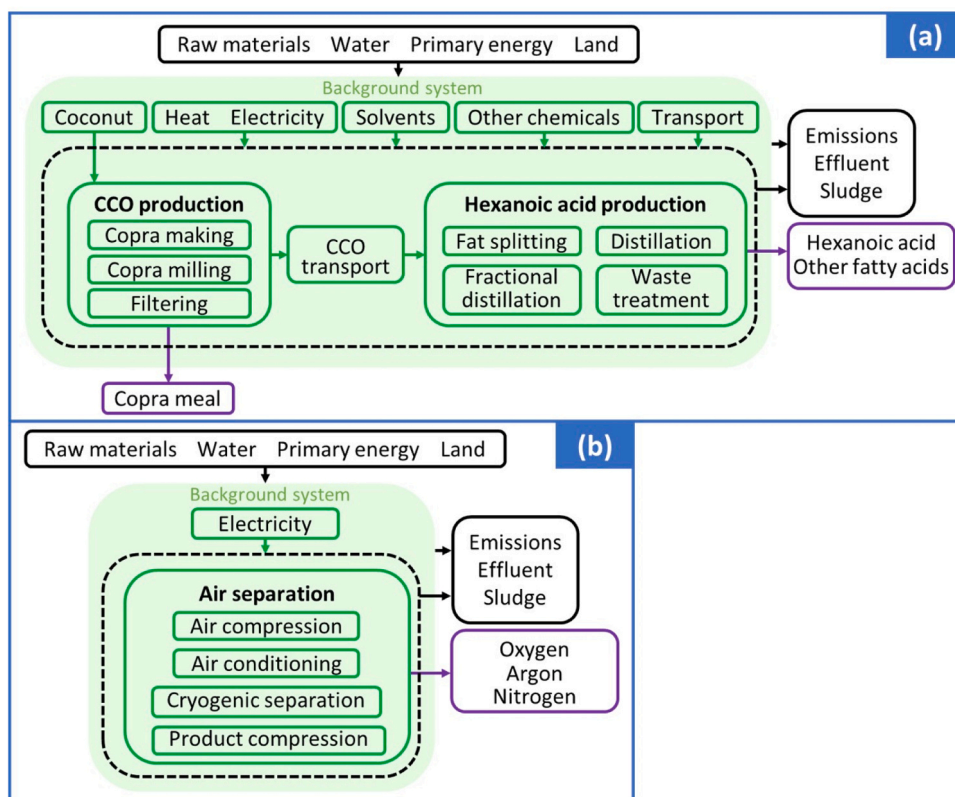


Fig. 3. System boundary of the reference system: (a) coconut-based hexanoic acid; (b) O₂ from an air separation unit.

2.2.2. Scenario II

2.2.2.1. System boundary. In this explorative scenario, the system boundary includes the transport of C6A to the neat SAF production plant (which was assumed to be 200 km away from the MES plant) and the production of neat SAF (see Fig. 4). The mass balance and emissions for the conversion of C6A to neat SAF were collected from literature [13, 14].

2.2.2.2. Functional unit and comparison to other studies. The functional unit was one MJ of neat SAF produced. It was calculated from the stoichiometry of converting C6A to neat SAF using the ratio 2.22 kg C6A:1 kg neat SAF [13,14] and the calorific value of average jet fuels, i. e., 43.4 MJ/kg [13,35] (check [supplementary materials](#) for details).

In this scenario, we focus on only one indicator, global warming potential (GWP; g CO₂eq/MJ neat SAF).

In contrast to scenario I, no reference system was explicitly modelled

in scenario II. Instead, the results of the current analysis were compared to the GWP of alternative neat SAFs produced from biomass, which were retrieved from the literature [21,36–38]. Since the referencing data might have different system boundaries, in the discussion (see Section 3.2.1), we included the final combustion emissions of conventional jet fuel for the neat SAF, which is 74 g CO₂eq/MJ [39] in addition to its cradle-to-gate system boundary to obtain a rough approximation of the cradle-to-grave direct GHG emissions, while recognising that emissions will be underestimated as transport of the product and any additional processes (e.g., storage) are not included. To the best of our knowledge, data on the LUC and iLUC emissions are not available for specific neat SAFs. For biofuels, the LUC and resulting iLUC emissions data are usually based on the biomass feedstock type, and data on converting the biomass feedstock to bioethanol or biodiesel is available in the literature [33,40]. This data was used for discussion purposes (see [supplementary materials](#) for details). Note that the neat SAF discussed in this work, neither MES- nor biomass-based SAF necessarily meets the regulated

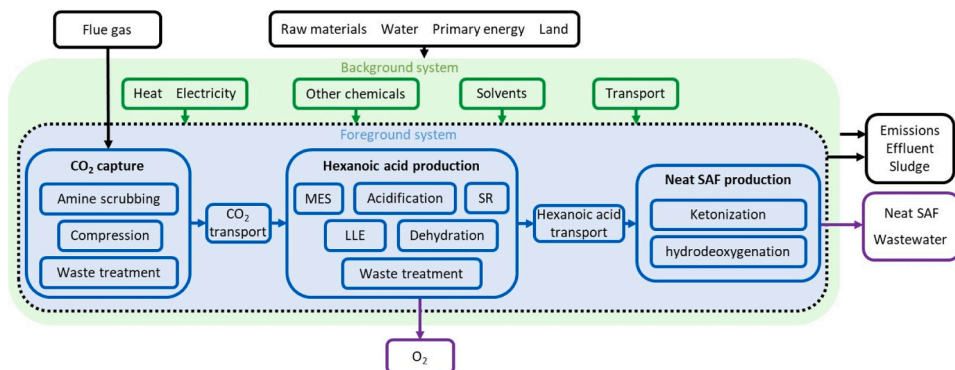


Fig. 4. System boundary of MES-based hexanoic acid in Scenario II. MES: microbial electrolysis. SR: solvent regeneration. LLE: liquid-liquid extraction. SAF: sustainable aviation fuel.

specifications. For the purpose of this study, it is assumed that they do.

2.2.2.3. Life cycle inventory. In addition to the LCI described in Section 2.2.1.4, data on C6A transport and neat SAF production were added to the LCI (see [supplementary materials](#)). Specifically, according to Huq [13], the emissions of neat SAF production activity are 15 g CO₂eq/MJ neat SAF.

3. Results and discussion

The LCA results are presented in Table 1. The results are discussed in the following sections.

3.1. Scenario I

3.1.1. Global warming potential

On a cradle-to-gate basis and when the economic allocation was applied, a tonne of C6A produced via MES generates about 5.5 t CO₂eq (see Table 1). Among the three activities (i.e., CO₂ capture, CO₂ transport and C6A synthesis) (see Fig. 5a), C6A production played a major role, accounting for 82 % of the total emissions. The top three emitters were utility generation, synthesis of other chemicals (i.e., H₃PO₄ and Ca(OH)₂), and electricity. It should be noted that even though renewable electricity has a lower carbon intensity than Dutch grid electricity, due to the large consumption in the C6A plant, the total emissions related to it were still considerable. As for the CO₂ capture activity, it contributed 18 % to the total carbon footprint, where utilities (steam) were the major emitter. The emissions resulting from short-distance CO₂ transport via pipeline were negligible in this study.

Table 1 also shows the importance of allocation on the final results, with substitution resulting in a lower GWP (16 %) than economic allocation. This difference represents the emissions saved by producing O₂ in the MES process instead of producing the same amount of O₂ in an ASU.

A comparison of the GWP of the MES route with the reference system and literature data. Table 1 shows that coconut-based C6A has a GWP at a similar level to the MES-based counterpart. We also compared the results to an alternative route (fermentation-based C6A). Three data points were found in [25]. They modelled the processes using a similar DSP configuration as in this work, namely LLE and SR. Their process used organic solid wastes at the lab and pilot scales. Two key differences in the LCA should be noted. First, the authors used gate-to-product system boundaries (equivalent to gate-to-gate), and second, they used mass allocation. The emissions ranged from 8.7 to 14.9 t CO₂eq/t C6A, with the pilot scale rendering the lowest emission. Note that in their

work [25], only the feedstock (i.e., organic solid wastes) was of non-fossil origin. The values of emissions of MES- and fermentation-based hexanoic acid are close. Considering the current technology readiness level of this MES (i.e., 2–3), differences in system boundaries, and differences in allocation methods, although MES seems to perform better, it is hard to assess which route outperforms the other regarding the GWP.

3.1.2. Land use

Fig. 5b shows the importance of other chemicals and electricity in the land footprint of the MES route. Note that H₃PO₄ alone made up 50 % of the share. In contrast to GWP, the allocation method did not have a significant impact on the results. When using substitution instead of allocation, the change in dLUC appeared insignificant. According to Ecoinvent's documentation for O₂ from an ASU in Europe, the dLUC is dominated by a small fraction of its electricity consumption that originates from combusting wood chips. Compared to the reference case, the dLUC of coconut-based C6A is 9335 m²a crop eq/t C6A, which is 20-fold higher than the MES-based plant. According to Alouw and Wulandari [41], the large land footprint of the reference might result from the low productivity of coconut in major exporting countries such as Indonesia and Malaysia.

As discussed previously, wind and solar farms can lead to iLUC. Fthenakis and Kim [42] reported 7.5 ~ 18.4 m²a/GWh for ground-mounted photovoltaic (PV) systems and 1.8–5.5 m²a/GWh for onshore wind farms. These values would correspond to 0.03–0.07 and 0.04–0.11 m²a/t C6A, respectively. Both values are, however, insignificant when compared to the dLUC (i.e., 416 m²a crop eq/t C6A).

The iLUC emissions in the MES system could also originate from wind and solar farms. According to Agostini [43], iLUC emissions associated with ground-mounted PV systems are less than 0.4 g CO₂eq/MJ electricity [44]. Converting it to our functional unit, it is equivalent to 0.006 t CO₂eq/t C6A, which is negligible compared to the direct GHG emissions (i.e., 5.5 t CO₂eq/t C6A). iLUC emission data on onshore wind farms are scarce. However, one could argue that iLUC emissions would be negligible as well because wind turbines must be installed with large spacings, and the free lands could be used [42].

To estimate the DLO of the MES plant, we used the combined DLO of a membrane electrolysis facility for chlorine production [45] and an ethanol plant that captures CO₂ from the flue gas of an adjacent steel plant and produces ethanol via fermentation [46]. The chloralkali plant has a capacity of 200 MW and occupies 0.32 km² of land (see [supplementary materials](#) for calculation details). The ethanol plant is also equipped with downstream separation and purification units. It has a volumetric capacity of 80,000 m³/y and occupies a land area of ca. 0.14 km² (see [supplementary materials](#) for calculation details). The MES plant has a nominal electricity capacity of 19 MW and a volumetric capacity of 10,900 m³/y. This rough calculation indicated that the DLO of the MES plant could remain below 1 km². Meanwhile, the DLO of the existing dedicated wind and solar farms in this scenario is estimated to be ca. 2.88 and 0.47 km², respectively (see [supplementary materials](#) for calculation details). Therefore, the land for the MES plant is smaller than the land needed for renewable electricity farms. In total, MES and electricity generation DLO is around 4 km². The fermentation route is operated at a pilot scale, and it is reported to occupy an area of 0.01 km² for 2 kt/y of >98 wt% medium-chain carboxylic acids (see [supplementary materials](#) for calculation details).

3.1.3. Water consumption

When using economic allocation, the MES system consumes about 122 m³/t C6A (see Fig. 6). H₃PO₄ contributed two-thirds of the total water consumption. The production of all the other chemicals made up about 70 % of total water consumption. The generation of renewable electricity accounted for 14 %. When substitution was applied, the results showed 50 % less water consumption. This can be explained because 50 % less water is consumed in the MES system to produce the

Table 1
Cradle-to-gate LCA results in Scenario I and II.

Scenario I	Global warming potential	Direct land use change	Water consumption
	t CO ₂ eq/t C6A	m ² a crop eq/t C6A	m ³ /t C6A
MES route			
With economic allocation	5.5	416	122
With substitution	4.6	407	61
Coconut route			
With economic allocation	5.0	9335	1202
Scenario II			
	Global warming potential		
	g CO ₂ eq/MJ neat SAF		
MES route			
With economic allocation	297		
With substitution	251		

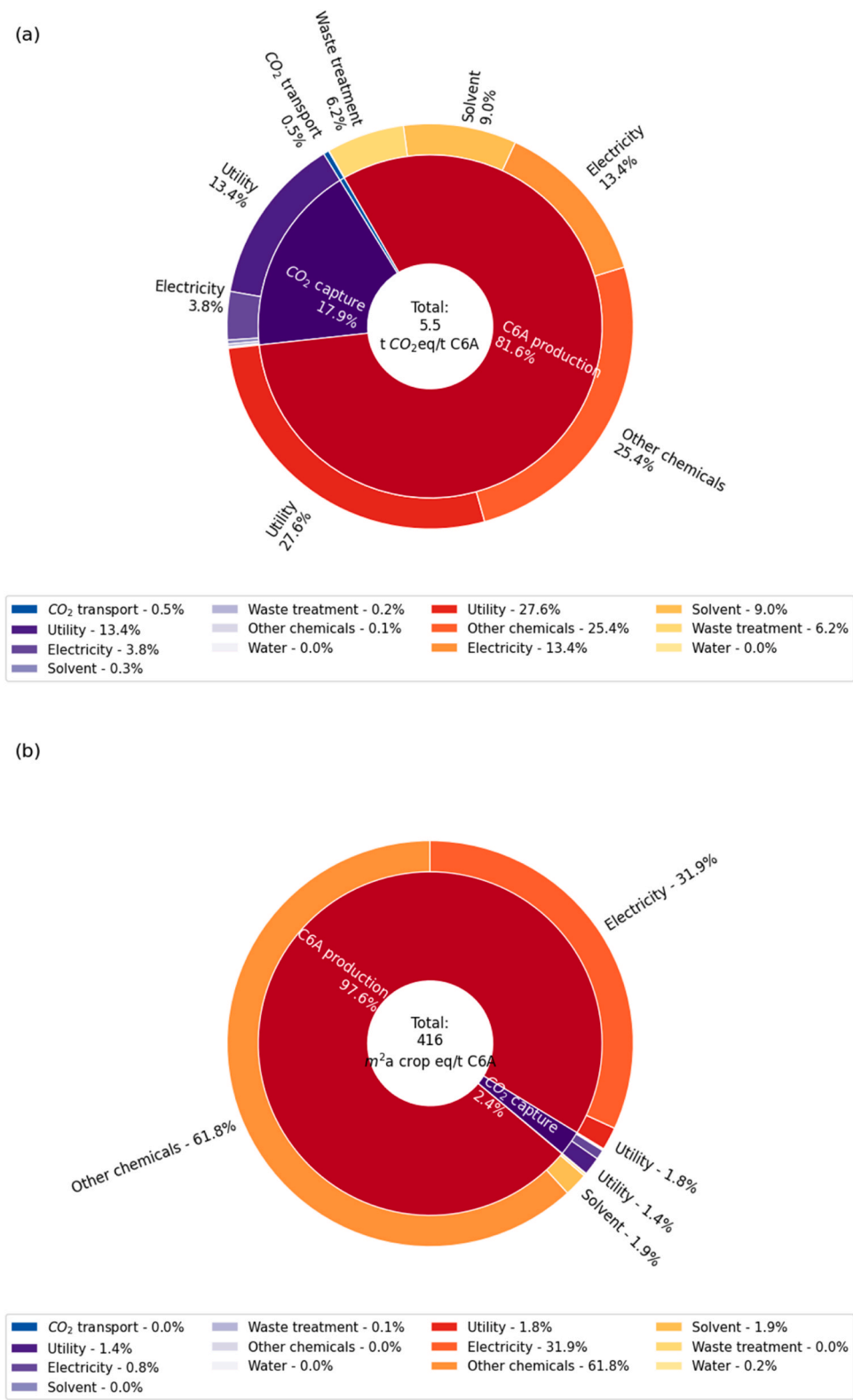


Fig. 5. Breakdown of the (a) GWP and (b) dLUC of the MES route with economic allocation. Small values are hidden from the pie chart but shown in the legend.

same amount of O₂ from an ASU. Note that coconut-based C6A uses 1202 m³/t C6A produced, equivalent to 10 times the water footprint of MES-based C6A. This point is further discussed in Section 3.1.4.

3.1.4. Sensitivity analysis

Given the importance of the utilities' contribution to the GWP, one-

at-a-time sensitivity analyses on electricity and heat (incl. chilling) energy were performed (see supplementary materials). If the carbon intensity of the grid electricity (consumed in the CO₂ capture and cooling water regeneration activities) were reduced by 90 %, the MES system's GWP could be lowered by 9 %. This is because electricity from the grid only accounts for 13 % of the GWP in the plant (the electricity used by

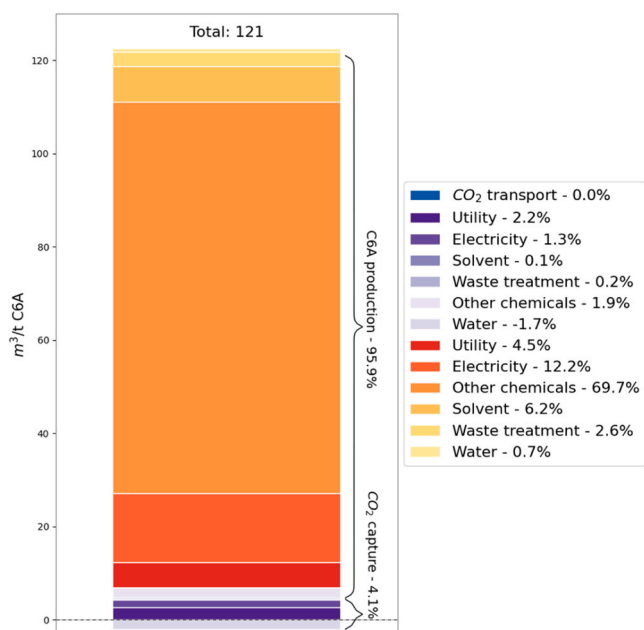


Fig. 6. Breakdown of water consumption of the MES route with economic allocation.

the electrolyser is mainly provided by a renewable plant). With a similar reduction in carbon intensity in the heat source (incl. chilling), the GWP could be lowered by 32 %. This indicates that defossilising the heat (incl. chilling) supply remains important in this kind of system.

The results of the sensitivity analysis on the carbon intensity of solvents and other chemicals show that changes in their carbon intensity are less significant. A 50 % change in the TEA's carbon intensity can lead to a 7 % variation in the final GWP, while the same change in the Al(OH)₃ carbon intensity can cause a 4 % variation (see [supplementary materials](#)).

Beyond the MES plant, it is important to highlight the large range of values found in literature, affecting the overall results. Coconut oil (CCO) has a GWP of 3.3 t CO₂eq/t CCO in Ecoinvent, while it is 6.7 t CO₂eq/t CCO in Agri-footprint. The difference gets even larger for other impacts. For instance, dLUC is 6510 m²a crop eq/t CCO in Ecoinvent and 20,000 m²a crop eq/t in Agri-footprint, while water consumption is reported as 840 m³/t CCO in Ecoinvent and 4.6 m³/t CCO in Agri-footprint. Based on the documentation in Ecoinvent inputs, the differences in water consumption could be linked to the quantity of irrigation water used and the allocation methods. Based on the information provided in the literature, pinpointing the cause of the differences was not possible, making a robust comparison of the technologies' relative performance difficult.

3.2. Scenario II

3.2.1. Global warming potential

The cradle-to-gate GWP of the neat SAF produced is significantly higher than that of the conventional route. This is independent of the allocation method used (297 g CO₂eq/MJ neat SAF when using economic allocation and 251 g CO₂eq/MJ neat SAF when using substitution). These values are 26-fold higher than conventional jet fuel (i.e., 9.6 g CO₂eq/MJ [39]). If we include the final combustion emissions of conventional jet fuel for the neat SAF, 74 g CO₂eq/MJ [39], the cradle-to-grave emissions will increase to 371 g CO₂eq/MJ neat SAF using economic allocation while 325 g CO₂eq/MJ neat SAF using substitution.

Since according to Huq [13], the neat SAF production activity, converting C6A to n-alkanes, only emits 15 g CO₂eq/MJ neat SAF, the

total cradle-to-gate emissions remained dominated by the production of C6A (see Fig. 7).

A comparison with literature data ([21] and references therein) on the GWP of different production routes of neat SAFs was performed. When neglecting the iLUC emissions and using substitution, the cradle-to-grave GWP of neat SAF produced through MES appears at least three times larger than most of its counterparts from alternative routes. Only when peatland rainforest or tropical forest is transformed into orchards that grow certain first-generation biomass (e.g., soybean oil and palm oil), will the substantial emissions caused by dLUC make the GWP of the neat SAFs produced from the first-generation biomass higher than the MES-based neat SAF [38]. The comparison with literature data is, however, not straightforward. For instance, using the guidelines for assessing emissions in the biofuel industry [47], avoided emissions can be counted as negative emissions, while the GHGs are not truly removed from the atmosphere. If the subtraction is significant, the impression can be given that the biofuel has a lower carbon footprint on a cradle-to-gate basis [48]. This point has been reported elsewhere, e.g. [13]. Second, the choice of the system boundary and the treatment of multi-functionality are not harmonised in the literature. Ng [21], for instance, estimated the CO₂eq emissions of a neat SAF derived from woody residues based on the emission data provided in [49]. The emissions in this study only included those from the CO₂ capture unit and did not include utilities or other activities on the supply chain. The same approach was used to estimate the emissions in [50]. Finally, in several cases, it is impossible to trace back how data was generated. Pavlenko [36], for instance, reported a carbon intensity of neat SAFs generated from municipal wastes at 14.8 g CO₂eq/MJ, which is only 40 % of the 37.5 g CO₂eq/MJ reported in the original source used for the estimation [48]. This points out a problem that goes well beyond the scope of this article regarding the harmonisation of system boundaries and allocation methods used in SAF literature.

3.2.2. Land use

The dLUC of the MES-based neat SAF is around 2 · 10⁻² m²a crop eq/MJ. The iLUC of wind and solar farms is negligible compared to the dLUC. dLUC and iLUC data for alternative non-SAF biofuels originating from various feedstock types can be found in [33,40] (see also [supplementary materials](#)). Among the studies in literature, the total LUC of the biofuel derived from agricultural residues is around 2.5 · 10⁻² m²a crop eq/MJ biofuel (= 2.5 ha/TJ) for agricultural residues, which is hence comparable to the MES-based neat SAF.

Regarding emissions from iLUC, as previously discussed in Section 3.1.2, the iLUC emissions of the MES route in Scenario I are likely to have limited impact. In Scenario II, although iLUC data on the upgrading process are lacking, it can be assumed to have a minor impact due to its efficient DLO and not use of biomass. Our reasoning for an efficient DLO is: 1) the upgrading reactions feature high yields and purities; 2) according to the process proposed by Huq [13], there are only seven unit operations involved, making it a relatively simple process route. Reported iLUC emissions of alternative biofuels can be found in [33,40] (see also [supplementary materials](#)). Bioethanol can be produced from different categories of biomass and has iLUC emissions in the range of 0–50 g CO₂eq/MJ. Biodiesel produced from energy crops and first-generation crops were assessed for iLUC emissions in both reports. Biodiesel derived from switchgrass, miscanthus, willow or poplar is reported to even lead to negative emissions, according to Valin [33], which is only possible at the gate. After the biodiesel is combusted, the carbon will be released, resulting in carbon neutrality at best, but not carbon negativity. For other feedstock, their iLUC emissions are above 50 g CO₂eq/MJ. Values are higher for neat SAFs from first-generation biomass, reaching up to 250 g CO₂eq/MJ. If these values are used as an indication for the iLUC emissions of alternative neat SAFs, the direct GHG plus iLUC emissions of neat SAF produced from first-generation biomass (e.g., palm oil and soybean oil) via the up-to-date most industrialised route (hydroprocessed esters and fatty acids-HEFA) can exceed

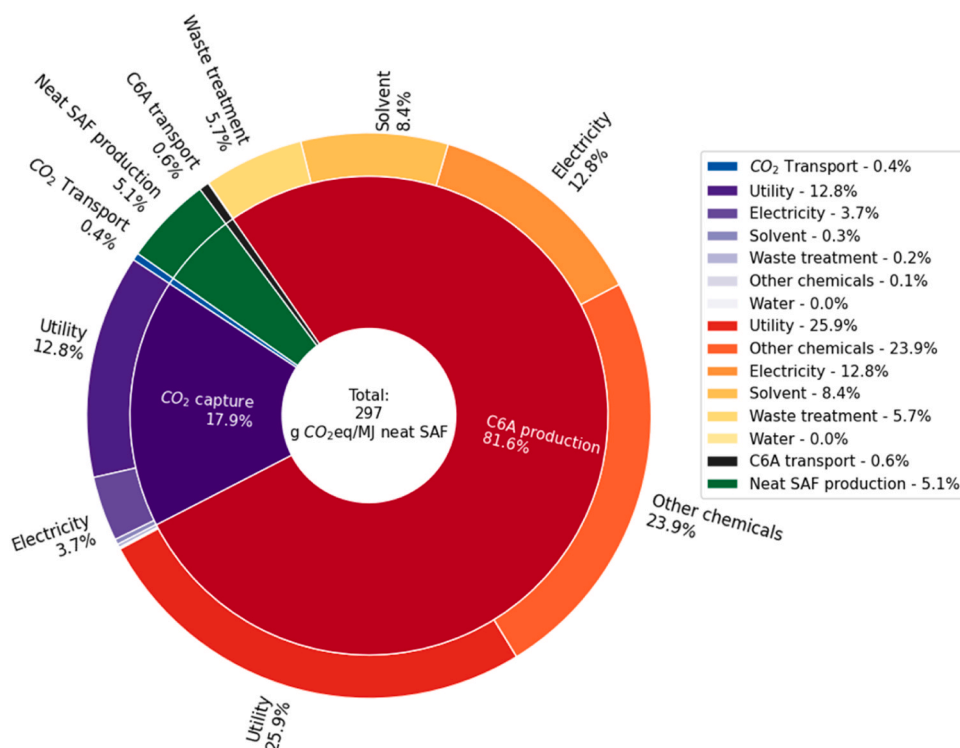


Fig. 7. Breakdown of the cradle-to-gate GWP and of the MES-based neat SAF with economic allocation. Small values are hidden from the pie chart but shown in the legend.

300 g CO₂eq/MJ on a cradle-to-grave basis. Thus, the neat SAF derived from MES-based C6A might be competitive.

4. Conclusion

This work assessed the environmental impacts of C6A produced via MES and renewable electricity and its derivative neat SAF and compared the results with other production routes. Cradle-to-gate assessments were performed to quantify global warming potential, land use, and water consumption of production systems. Both economic allocation and substitution were applied to examine the multifunctionality of the MES production system.

When an economic allocation was applied, the results showed that the GWP of C6A produced from CO₂ via MES is comparable to the GWP of C6A produced from coconut oil via fractional distillation and from organic solid wastes via fermentation. Factors that would reduce the carbon footprint of the MES route are defossilising heat and chilling utilities used in energy-intensive downstream processing as well as using less carbon-intensive chemicals.

The results also highlight the advantage of MES in terms of land use, as it is 20 times lower than the reference case (coconut-based hexanoic acid). Additionally, the direct land occupation of the renewable electricity farms is likely larger than the MES plant itself. The major shares in both land use and water consumption of the MES route are due to the vast consumption of renewable electricity in the C6A production activity and the chemicals used in the C6A production activity, especially H₃PO₄, for its large consumption of fossil resources. The overall picture indicates that the MES-based C6A has a lower environmental impact than the coconut-based C6A.

If C6A produced via MES is further upgraded to produce neat SAF, the GWP of this route does not seem to outperform alternative routes, with the exception of iLUC emissions. A reliable comparison with published LCA studies on biomass-based SAF production is currently difficult due mainly to differences in system boundaries. Nonetheless,

considering the direct CO₂eq emissions and iLUC emissions together, neat SAF derived from MES-based C6A might be competitive with counterparts that use first-generation biomass. However, there are alternative neat SAFs with a lower carbon intensity being developed and industrialised. Finally, for future research, the conversion of C6A produced via MES to other chemicals, such as adipic acid, should be explored.

CRedit authorship contribution statement

Adrie J.J. Straathof: Writing – review & editing, Validation, Funding acquisition. **Andrea Ramirez:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Jisiwei Luo:** Writing – original draft, Visualization, Software, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Mar Pérez-Fortes:** Writing – review & editing, Validation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Life cycle inventory

A1. MES route

Table S4

LCI of the MES-based hexanoic acid route. MEA: Monoethanolamine. GLO: global. RER: Europe. NL: Netherlands. AP: Aspen Plus. TOA: trioctylamine. BE: Belgium.

Input	Quantity	Unit	Source	Ecoinvent data source
CO ₂ capture				
Solvent – MEA	2.32	kg/t CO ₂ captured	[51]	Monoethanolamine market for GLO
Electricity – grid (for process incl. compression)	0.57	GJ/t CO ₂ captured	[51]	Electricity, medium voltage market for NL
Water – tap (for process)	1000	kg/t CO ₂ captured	[51]	Tap water market group for RER
Other chemicals – NaOH	2	kg/t CO ₂ captured	¹ assumed based on [52]	Sodium hydroxide, without water, in 50% solution state market for GLO
Utility – heat (by natural gas)	3.72	GJ/t CO ₂ captured	[51]	Heat, district or industrial, natural gas market group for RER
Utility – grid electricity (for regenerating cooling water)	0.81	GJ/t CO ₂ captured	[53]	Electricity, medium voltage market for NL
Utility – cooling water	68.3	kg/t CO ₂ captured	[53]	Tap water market group for RER
Waste treatment – sludge (incl. waste solvent)	2.32	kg/t CO ₂ captured	² assumed based on [52]	Refinery sludge Europe without Switzerland treatment of refinery sludge, hazardous waste incineration, with energy recovery
Waste treatment – wastewater	1000	kg/t CO ₂ captured	³ assumed based on [51]	Wastewater, average Europe without Switzerland market for wastewater, average
CO ₂ compression loss	0%		assumed	
CO ₂ transport				
Transport – pipeline	200	km	⁴ assumed	Transport, pipeline, onshore, long distance, natural gas RER market for transport, pipeline, offshore, long distance, natural gas
Hexanoic acid production - MES				
Captured CO ₂	2272	kg/t C6A produced	⁵ AP simulation	
Water – demineralised (for process)	3686	kg/t C6A produced	AP simulation	Water, completely softened RER market for water, completely softened
Other chemicals – Ca(OH) ₂	473	kg/t C6A produced	AP simulation	Aluminium hydroxide market for GLO
Other chemicals – H ₃ PO ₄	708	kg/t C6A produced	AP simulation	Phosphoric acid, industrial grade, without water, in 85% solution state market for GLO
Solvent – TOA	213	kg/t C6A produced	AP simulation	Trimethylamine market for RER
Electricity – wind (for process)	68.9	GJ/t C6A produced	AP simulation	Electricity, high voltage NL electricity production, wind, >3MW turbine, onshore
Electricity – solar (for process)	14.1	GJ/t C6A produced	AP simulation	Electricity, low voltage BE electricity production, photovoltaic, 570kWp open ground installation, multi-Si
Utility – heat (by natural gas)	22.6	GJ/t C6A produced	AP simulation	Heat, district or industrial, natural gas market group for RER
Utility – cooling water	228	kg/t C6A produced	AP simulation	Tap water market group for RER
Utility – chilling energy (by natural gas)	6.09	GJ/t C6A produced	AP simulation	Cooling energy market for GLO
Utility – grid electricity (for regenerating cooling water)	0.041	GJ/t C6A produced	AP simulation	Electricity, medium voltage market for NL
Waste treatment –sludge	824	kg/t C6A produced	AP simulation	Waste gypsum Europe without Switzerland treatment of waste gypsum, inert material landfill
Waste treatment – wastewater	2629	kg/t C6A produced	AP simulation	Wastewater from vegetable oil refinery market for GLO
Waste treatment – spent solvent	213	kg/t C6A produced	AP simulation	Spent solvent mixture Europe without Switzerland market for spent solvent mixture

¹The weight ratio between NaOH and captured CO₂ was 1:1 in the reference, but we assumed it to be 2:1.²It was assumed in the reference that the weight ratio between the monoethanolamine and sludge disposal was 1:1.³It was calculated based on the process data provided in the reference and made a slightly optimistic approximation.⁴It was assumed that the plant was 200 km within the CO₂ pipeline network in Port of Rotterdam.⁵Aspen simulation refers to the results from [26]Luo, J., et al., Understanding the flexibility challenges of a plant for microbial CO₂ electroreduction with hexanoic acid recovery, unpublished results. 2024.

A2. Coconut route

Table S5

LCI of the coconut-based hexanoic acid. RER: Europe.

Input	Quantity	Unit	Source	Ecoinvent data source
Hexanoic acid production – from coconut oil				
Fatty acid	1000	kg/t C6A	[28]	Fatty acid RER fatty acid production, from coconut oil

A3. Crude coconut oil production

Table S6

LCI data of the crude coconut oil production. RER: Europe. GLO: global.

Database	Data source
Agri-footprint	Crude coconut oil, mart mix, at regional storage RER
Ecoinvent	Coconut oil, crude market for GLO

A4. Sustainable aviation fuel

Table S7

LCI of the upgrade of hexanoic acid to n-alkanes.

Input	Quantity	Unit	Source	Ecoinvent data source
Hexanoic acid transport				
Transport-truck	200	km	¹ assumed	Transport, freight, lorry 16-32 metric ton, euro6 RER market for transport
Upgrading to neat SAF				
Hexanoic acid	2.22	kg/kg neat SAF	[13,14]	
Emissions (gate-to-gate)	15	g CO ₂ eq/MJ neat SAF	[13]	

¹It was assumed that the neat SAF plant was 200 km away from the MES plant.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2024.113924](https://doi.org/10.1016/j.jece.2024.113924).

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