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Towards aromatics from biomass: Prospective Life Cycle Assessment of bio-based aniline

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ABSTRACT

Bio-based chemicals are seen as a potential stepping-stone towards a more sustainable chemical industry. However, while bio-based routes are already available for various organic alcohols and acids, the direct bio-based production of aromatic compounds has been difficult so far. Recently, the first bio-based process for the production of the important aromatic aniline has been realized. The process produces bio-based aniline via two-stages: first, sugar is fermented by *Corynebacterium Glutamicum* to aminobenzoic acid, which is then catalytically decarboxylated to aniline. In this study, we present a prospective Life Cycle Assessment for bio-based aniline production to evaluate the environmental potential compared to fossil-based aniline production. Our results suggest that the bio-based production could reduce the global warming impacts of aniline from cradle-to-grave by 35–69% relative to fossil-based production, depending on the type of biomass feedstock. However, bio-based aniline could also substantially increase eutrophication and acidification, a trade-off commonly observed for bio-based processes. Thus, the novel production route is promising and expands the scope of bio-based chemicals towards aromatics.

1. Introduction

The drive to lower carbon emissions and less reliance on fossil feedstocks forces the chemical industry to look for new carbon sources. Here, bio-based carbon sources could offer an alternative to fossil-based feedstocks (Hermann et al., 2007). This development is reflected by steady growth predictions for the bio-based chemical industry by around 3.6% annually between 2020 and 2025 in the EU (Spekreijse et al., 2019), and the increasing number of bio-based processes for the production of aliphatic chemicals discussed in the literature. Recent developments include bio-based production of 1,4-butanediol (Balat and Balat, 2009; Burgard et al., 2016), 2,3-butanediol (Celińska and Grajek, 2009), adipic acid (Aryapratama and Janssen, 2017), butadiene (Cespi et al., 2016), ethylene (Morschbacker, 2009), lactic acid (Datta and Henry, 2006), methanol (Eggemann et al., 2020), sorbitol (Moreno et al., 2020) and succinic acid (Bechthold et al., 2008).

Aromatic compounds are key platform chemicals required in a wide variety of products ranging from polymers to pharmaceuticals. However, bio-based production of aromatic chemicals remains challenging, though some routes are emerging (Jiang et al., 2020; Lin et al., 2015). Significant progress has been made in the depolymerization of lignin into aromatic chemicals (Zakzeski et al., 2012; Rahimi et al., 2014). Nevertheless, its complex structure and high stability still render lignin a challenging feedstock (Zhang and Wang, 2020; Chen et al., 2016). In contrast, sugars are known as efficient feedstock for bio-based processes. However, no large-scale processes for producing aromatic chemicals from sugar were available until recently (Kawaguchi et al., 2016; Krömer et al., 2020). This limitation has been overcome with the development of the first process for the bio-based production of the aromatic compound aniline via fermentation of sugar (Jaeger et al., 2017).

Aniline is a vital intermediate in the production of polyurethanes and has a global production volume of 5000 kt per year (IHS Markit, 2017). The fossil-based production of aniline emits around 25 Mt of CO_2 and consumes 0.3 EJ of non-renewable energy yearly. These environmental impacts could be reduced by the new

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bio-based process and, in extension, reduce the impact of a wide range of polyurethane products, such as isolation panels and mattresses (von der Assen and Bardow, 2014; Meys et al., 2019).

However, while many bio-based chemicals have been shown to reduce global warming impacts compared to fossil-based products, environmental benefits cannot be taken for granted and depend on many factors (Spierling et al., 2018). These factors range from the substituted product over the type of bio-based feedstock to the region of production (Muñoz et al., 2014). For instance, bio-based lactic acid and ethylene have been reported to reduce global warming impacts compared to fossil-based production for a variety of bio-based feedstocks (Weiss et al., 2012). Papong et al. show that bio-based PLA bottles offer advantages compared to fossil-based PET bottles (Papong et al., 2014). Bio-based butadiene, however, only reduces global warming impacts when produced from low-impact feedstocks (Cespi et al., 2016). Additionally, the production of bio-based chemicals often increases environmental impacts related to agriculture, such as acidification and eutrophication (Weiss et al., 2012; Brentrup et al., 2004).

The literature reviewed shows that a full understanding of the benefits and drawbacks of the new bio-based aniline production process requires a careful evaluation of multiple environmental impacts, regions of production, and types of bio-based feedstocks. Such an analysis can be carried out with the method of Life Cycle Assessment (LCA), a standardized method to evaluate the environmental impacts of products, product systems, and services (DIN EN ISO, 2006).

In this work, we provide a prospective LCA study for a new and first of its kind bio-based aniline production process. We calculate the potential environmental impacts of bio-based aniline in the regions with the largest aniline demand: the USA, the EU, and Asia (IHS Markit, 2017), including all life cycle activities for bio-based aniline, the cultivation of feedstock, the transport to the production facility, and the production of aniline. Finally, the environmental impacts of bio-based aniline are compared to fossil-based aniline.

2. Aniline production

Aniline is an aromatic chemical consisting of a phenyl group with an attached amino group. Aniline was first discovered in 1826 and has since found many applications for the production of dyes, pharmaceuticals, and polymers. Currently, the majority of aniline is produced from fossil resources. (Ullmann's, 2010).

Fossil-based aniline is produced in two reaction steps from benzene. First, benzene is nitrated to nitrobenzene with nitric acid. Nitrobenzene is separated from unreacted benzene via distillation. Second, the nitrobenzene is hydrogenated to aniline at nearly complete conversion and then dried by distillation drying. During hydrogenation of nitrobenzene, a large amount of excess heat is generated that can be used in other processes.

However, recently, a bio-based alternative to fossil-based production has been developed (Jaeger et al., 2017). In this new process, sugar is first fermented to aminobenzoic acid (AB), which is then reacted to aniline (Fig. 1).

In the first step of the process, sugar and ammonia are fermented to aminobenzoic acid by a genetically engineered strain of *Corynebacterium Glutamicum* (Eq. (1)).

$$\text{Sugar} + \text{Ammonia} \xrightarrow{ferment.} \text{Aminobenzoic Acid} + CO_2 + \text{Biomass} \quad (1)$$

Sodium hydroxide is added to the fermenter to neutralize the aminobenzoic acid and to stabilize the pH value. The fermentation broth leaving the fermenter is filtered, and the cells are separated. Excess cells are incinerated to supply process energy. The filtered fermentation broth continues to the separation section, where the aminobenzoic acid is precipitated in a pH-shift crystallization. The pH value of the solution is lowered below 4 by adding hydrochloric acid. As a result of this low pH, the solubility of aminobenzoic acid in water drastically decreases to approximately 0.5 wt-%, inducing crystallization of aminobenzoic acid. To increase the overall yield, the depleted aminobenzoic acid solution leaving the pH-shift crystallization is enriched in an adsorption/desorption column and recycled to the crystallization.

After the crystallization, the aminobenzoic acid crystals are dissolved in a solvent (e.g. 1-dodecanol or aniline). The aminobenzoic acid solution is then heated to an elevated temperature where the aminobenzoic acid decomposes into the desired product, aniline and carbon dioxide, optionally using a catalyst, with nearly complete conversion (Eq. (2)).

$$C_7H_7NO_2 \rightarrow C_6H_5NH_2 + CO_2 \quad (2)$$

After the reaction, side components are separated from aniline by distillation, yielding above 99% purity.

3. Methodology and data

In this section, we describe methodological choices of our LCA study regarding goal and scope definition, functional unit, system boundaries, as well as indirect land-use change, and feedstock availability. Inventories and further data are available in the SI.

3.1. Goal and scope definition

LCA aims at a holistic evaluation of the environmental impacts caused by a production system, taking into account its complete life cycle (DIN EN ISO, 2006). The goal of the presented LCA study is to compare potential environmental impacts of bio-based aniline production to conventional fossil-based aniline production. For this purpose, we apply a cradle-to-gate system boundary considering all activities to either produce bio- or fossil-based aniline: from the extraction of resources up to the factory gate. A cradle-to-gate system boundary is sufficient to compare bio- and fossil-based aniline since aniline from both routes is chemically identical, and thus no difference is expected in the subsequent life cycle stages (von der Assen et al., 2013; von der Assen et al., 2014).

However, special attention should be paid to the accounting of biogenic carbon. The literature proposes two approaches to account for biogenic carbon (Pawelzik et al., 2013). The first approach, popular for bio-fuels, is to neither account for biogenic carbon uptake nor its release. This approach is based on the idea that as long as the final product is eventually combusted, biogenic uptake and release are equal and thus do not need to be accounted for. The second approach is to account for biogenic carbon emissions at all stages of the life cycle. In this approach, carbon uptake from the atmosphere results in negative emissions, while the release of biogenic carbon, for instance, during fermentation, results in positive emissions. If cradle-to-grave system boundaries are applied, and the end-of-life scenario is eventual combustion, both approaches lead to the same results (Pawelzik et al., 2013). In this study, we follow the second approach and account for all carbon streams. However, to increase readability and focus on bio-based aniline production, we aggregate all biogenic streams during sugar production and thus only consider the net carbon uptake of sugar.

When taking carbon uptake into account, cradle-to-gate system boundaries can result in negative global warming impacts. These

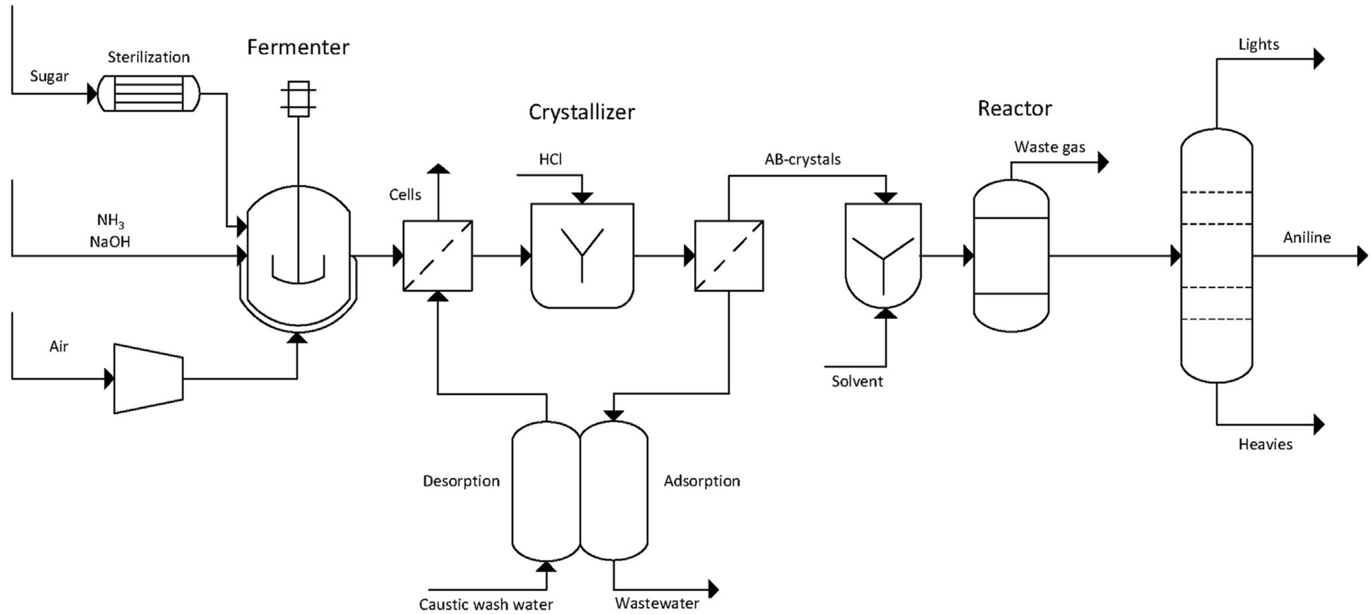

Fig. 1. Process flowsheet of bio-based aniline production from glucose and ammonia via fermentation with *Corynebacterium Glutamicum*.

negative impacts can lead to misinterpreting bio-based aniline as a carbon-negative technology. However, whether bio-based aniline is carbon-negative or not depends on the full life cycle. If the carbon is released at the end of life, carbon emissions can be neutral at best (Tanzer and Ramírez, 2019). To avoid any potential confusion between carbon-negative and carbon-neutral technologies, we include the release of stored CO_2 without energy recovery as end-of-life, which leads to positive life cycle global warming impacts but has no effect on the other impact categories. Thus, we use cradle-to-grave system boundaries for global warming impacts and cradle-to-gate system boundaries for all other impact categories.

Many LCA studies have shown that environmental impacts of bio-based chemicals and fuels depend strongly on the type of feedstock, which varies between world regions (Muñoz et al., 2014; Renouf et al., 2008). We, therefore, consider three regions and four feedstocks: (1) US, with corn and corn stover, (2) EU with sugar beet, and (3) Asia with sugar cane. These three regions are selected, as they produce the majority of the global aniline (IHS Markit, 2017). The focus on regions with high aniline production leads to the exclusion of Brazil, often considered as a promising country for bio-based production (Lossau et al., 2015). The feedstocks are selected to include one of the major feedstocks for fermentable sugar production in every region. At the same time, the feedstocks represent different types, ranging from starch and sucrose to second-generation lignocellulosic feedstocks. Thereby, a wide variety of feedstocks is covered.

Bio-based processes often shift environmental burdens away from global warming towards other impact categories, in particular to eutrophication and acidification (Brentrup et al., 2004). Thus, this LCA study assesses global warming impacts, but also abiotic depletion, eutrophication, acidification, and photochemical ozone creation potential. We choose CML2001/2016 (Guinée, 2002) as impact assessment method, as this method is recommended for product environmental footprints (European Comission, 2016).

In the main discussion, we focus on global warming and fossil depletion, as reductions in these categories are seen as the main driver for the development of bio-based processes. In our discussion of the global warming impacts, we explicitly include the effects of indirect land-use change, which can be significant (Searchinger et al., 2008). To quantify potential burden-shifting, we also analyze acidification and eutrophication. Photochemical ozone creation potential is not discussed in the main paper but is available in the SI. Environmental impacts are calculated using the software GaBi ts V8.7. Regionalized datasets are used for the US, the EU, and Asia when available. If not, data from the US is used as a proxy. A full list of all background processes is available in the SI.

3.2. Functional unit

The goal of this study is the environmental assessment of bio-based aniline production. Therefore, the functional unit of this LCA study is defined as 1 kg of aniline.

While the primary aniline production process yields no by-products, the production of sugar, the primary feedstock for bio-based aniline, produces several by-products. The ISO norm and LCA guidelines recommend using system expansion for multi-functional systems, which, however, does not provide product-specific impacts (DIN EN ISO, 2006; Zimmerman et al., 2018). For comparative LCA, system expansion is mathematically identical to substitution (also called avoided burden), as both approaches yield the same changes in environmental impacts (von der Assen et al., 2013). In this study, we, therefore, deal with by-products by substitution. The effect of substitution on the environmental impact of feedstock production is further discussed in the SI, where the environmental impact of aniline production is assessed, assuming no substitution effects.

3.3. System boundaries

3.3.1. Production system for bio-based aniline

The bio-based production of aniline can be divided into two parts (Fig. 2): (1) sugar production and (2) aniline production.

The focus of this LCA study is to analyze the potential environmental impact of bio-based aniline production. However, since the supply of fermentable sugar has the largest share in the overall environmental impact of bio-based aniline production, we describe the fundamental assumptions for sugar production in this section.

3.3.1.1. *Sugar production.* The environmental impact of sugar varies strongly with its feedstock (Renouf et al., 2008). To show the extent of this variation, we consider the production of different feedstocks in the three regions of high aniline production. We consider the following feedstocks: corn and corn stover in the US, sugar beet in the EU, and sugar cane in Asia.

The system boundaries of sugar production include all activities involved in the cultivation and harvest of the biomass, as well as transport and refinement to fermentable sugar. Feedstock processing is assumed to take place next to the aniline production plant. Therefore, no transport is considered for refined sugar. Detailed system boundaries and full inventories are available in the SI. (See S1).

For the US, corn is assumed to be produced in the corn belt, the largest corn-producing region in the US (Kim et al., 2009). Corn is processed by wet milling to yield fermentable sugar (Renouf et al., 2008). The wet-milling process yields a number of high-value by-products: corn oil, corn gluten meal, and corn gluten feed. These by-products can be used to substitute the production of soy oil, soybean meal, and corn, respectively (Renouf et al., 2008).

Corn stover is a by-product of corn production. Currently, most corn stover is left on the field after harvest to improve soil properties and curb wind erosion (Wilhelm et al., 2004). Only a small fraction is collected for animal bedding. According to Graham et al. around 50% of corn stover could be collected without compromising soil properties (Graham et al., 2007). Due to its high availability in the US and its current lack of use, corn stover has been identified as a promising feedstock for bio-based production of fuels and chemicals (Kadam and McMillan, 2003). In this LCA study, we treat corn stover as a waste product with no economic value. Therefore, no impacts from corn cultivation are attributed to the corn stover. Only the impact of activities linked to stover collection, such as additional energy demand, fertilizer to compensate removed nutrients, and the carbon uptake of corn stover, are attributed to the corn stover. The collected corn stover is processed by deacylation and dilute acid pretreatment, followed by hydrolysis to yield fermentable sugars (Davis et al., 2498). All data on this processing technology is available on the NREL website (NREL, 2018). The lignin fraction of corn stover is burned to provide heat and electricity for the process. The produced electricity exceeds the demand of the sugar-processing plant and is assumed to substitute the average regional electricity mix.

For the EU, sugar beet cultivation and processing are modeled based on Renouf et al. (2008). Due to the availability of background data, production is assumed to take place in Germany. The extraction of sugar from sugar beets yields beet pulp as by-product. This excess beet pulp can be used as animal feed and is assumed to substitute barley (Renouf et al., 2008).

In Asia, sugar production is modeled based on a survey of sugar cane farmers in north-eastern Thailand conducted by Prasara-A et al. (Prasara-A and Gheewala, 2016). Thailand is one of the largest regional producers of sugar cane (FOA, 2019) and has already established the bio-based production for ethanol and lactic acid (Groot and Borén, 2010). The large supply of sugar and the existing bio-based industry makes Thailand a promising candidate for aniline production in Asia. Prasara-A et al. report very high use of phosphate fertilizers in the cultivation of sugar cane in Thailand. This fertilizer use is in line with fertilizer use in India, but much larger than in Brazil, and negatively affects the environmental performance of Thai sugar cane (Tsiropoulos et al., 2014, 2015). According to Prasara-A et al., this high use of fertilizer may not increase the yield, and environmental impacts of sugar production could be lowered by better fertilizer management (Prasara-A and Gheewala, 2016). Sugar mills generally burn excess sugar cane bagasse to supply heat and electricity to the sugar mill. While some mills also export excess electricity to the grid or supply heat to nearby processes, we assume no electricity or heat export in this study to get a conservative approximation. The possibility of heat export is considered in the SI.

The different feedstocks used for sugar production lead to different types of sugars: Corn yields glucose, sugar beet and sugar cane yield sucrose, and corn stover a mix of C5 and C6 sugars. We

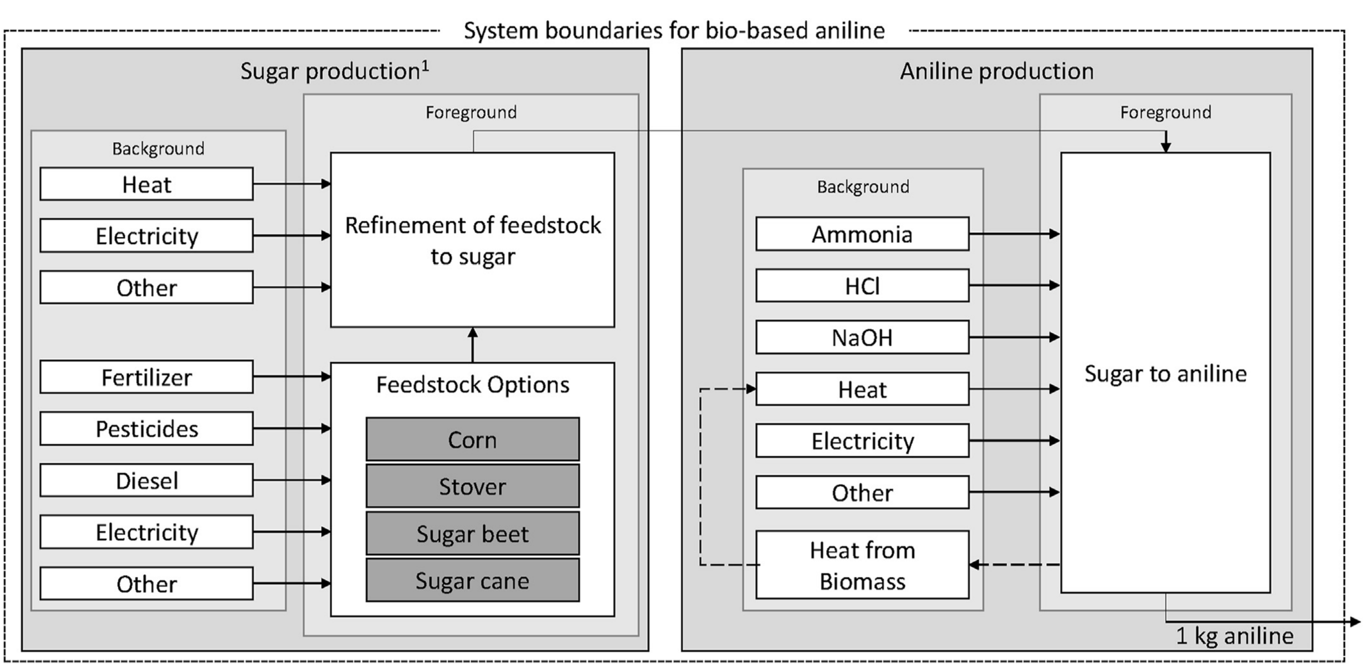

Fig. 2. Cradle-to-gate system boundaries of bio-based aniline production. The system contains two subsystems: 1) the production of fermentable sugar and (2) aniline production by fermentation and reaction of sugar. Sugar production contains multiple feedstock options. System boundaries for each feedstock option are shown in the SI.

assume that the strain of *Corynebacterium Glutamicum* used in the bio-based aniline process can be modified to ferment all kinds of sugar equally well. Achieving high yields simultaneously from C5 and C6 sugars might prove challenging, but the theoretical yield of bio-based aniline shows only little difference between C5 and C6 sugars (Jaeger, 2018) and high yields in the simultaneous fermentation of C5 and C6 sugars have already been achieved for ethanol (Saha et al., 2015).

3.3.1.2. Indirect land-use change. Indirect land-use change (iLUC) has been identified as a major drawback of bio-based feedstocks by Searchinger et al. (2008). Following this publication, a number of governmental agencies and research groups worked on improving our understanding of iLUC, though uncertainty remains (Plevin et al., 2010). Since indirect land-use change can contribute significantly to global warming impacts of bio-based chemicals, iLUC should be considered in the LCA of bio-based products (Pawelzik et al., 2013).

To quantify the potential impact of indirect land-use change, we adapt values for indirect land-use change of ethanol production to our aniline case study. Since there are numerous studies for land-use change available with differing results, we include multiple studies for each feedstock to show the resulting uncertainty. The largest number of studies is available for corn (California Air Resources Board, 2016; Broch et al., 2013; Dunn et al., 2013; Tyner et al., 2010) and sugar-beet-based ethanol (Al-Fiffai et al., 2010; Marelli et al., 2011; Laborde, 2011; Darlington et al., 2013), while two studies report on corn-stover-based ethanol (Dunn et al., 2013; Taheripour and Tyner, 2012). To our knowledge, no studies specifically report the indirect land-use change of Thai sugarcane cultivation, though some report land-use change for sugar cane in general (Al-Fiffai et al., 2010; Marelli et al., 2011; Laborde, 2011). We included values from these studies as a proxy for Thai sugarcane cultivation. However, these results should be treated with caution. The environmental impact of indirect land-use change from the considered studies also include any direct land-use change, as the models used for the calculation of land-use change do not differentiate between direct and indirect land-use change. Following the naming scheme of the majority of these publications, we still call the combined effect indirect land-use change.

3.3.1.3. Bio-based aniline. To compare the bio-based process to fossil-based production, Covestro Deutschland AG (Covestro) provided us with the results of process simulations for the bio-based process conducted in the commercial flowsheeting tool Aspen Plus®. These simulations calculate the energy and material requirements for an industrial-scale process. Each step of the bio-based process has already been proven in lab- or pilot-scale by Covestro (Jaeger, 2018). Thus, the present LCA is prospective to evaluate the potential benefits and downsides from an up-scaled and optimized industrial process.

3.3.2. Production system for fossil-based aniline

The inventory data for the nitration of benzene to nitrobenzene and the hydrogenation of nitrobenzene to aniline is based on data from IHS Markit. Both reactions have a yield greater than 98%. The excess heat from the nitration is used to substitute steam production from natural gas. The background data is taken from the LCA databases GaBi ts (thinkstep, 2019) and ecoinvent (Wernet et al., 2016) (Fig. 3). The environmental impact of fossil-based aniline is calculated only for the regions EU and US but not for Asia due to lack of background data for this region.

4. LCA results and discussion

The environmental impact of the production of 1 kg aniline is calculated in the three regions, US, EU, and Asia, with the feedstocks, corn (US), corn stover (US), sugar beet (EU), and sugar cane (Asia). First, we compare bio-based aniline produced in the US using corn as feedstock to fossil-based aniline in order to examine the impacts of the individual activities in detail. Afterward, the sensitivity of the results towards different feedstock options and land-use change are analyzed. Finally, the demand and availability of feedstock are discussed.

4.1. Environmental impacts for aniline from US corn

In the US, around 40% of the annual corn harvest is already used for bio-ethanol production (DOA, 2018). Due to this massive scale, the processing of corn to sugar is a well-established industry. Therefore, we use the US as a base-case to discuss the difference in environmental impacts between bio-and fossil-based aniline production.

4.1.1. Global warming impact

From cradle-to-grave, the global warming impacts of bio-based aniline amount to 3.9 kg CO_2 eq/kg aniline with corn as feedstock in the US (Fig. 4). The global warming impacts of fossil-based aniline are 6.0 kg CO_2eq/kg aniline. Thus, the bio-based process could reduce cradle-to-gate emissions by 34%, assuming that all aniline-based products are eventually combusted.

The production of the fundamental feedstock sugar has a net uptake of carbon of 4.7 kg CO_2/kg aniline. Of this 4.7 kg CO_2, 1.8 kg are released during the fermentation and decarboxylation. As a result, 2.8 kg of CO_2 are stored in the bio-based aniline. This carbon is eventually released at the end-of-life leading to net-zero biogenic carbon emissions over the whole life cycle.

Production of bio-based aniline also creates non-biogenic CO_2 emissions which are 3.9 kg CO_2eq/kg aniline in total. Sugar

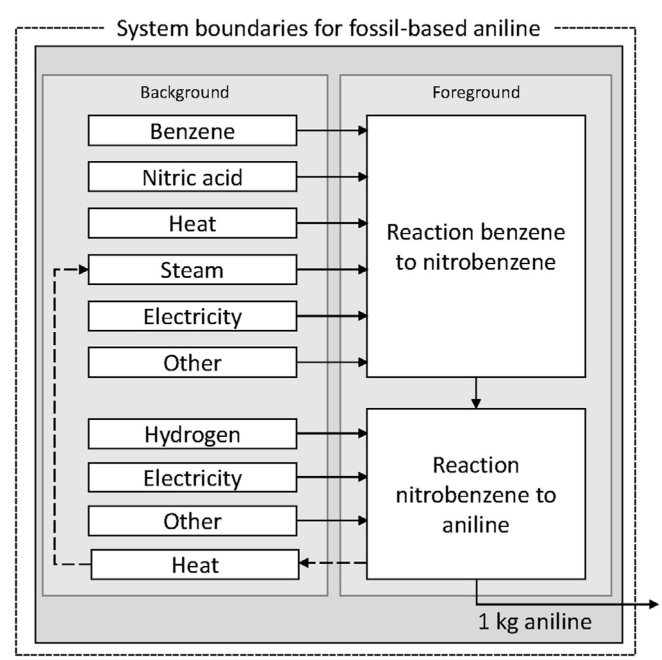

Fig. 3. Cradle-to-gate system boundaries of fossil-based aniline production. Production of aniline takes place by nitration of benzene to nitrobenzene, followed by hydrogenation of the nitrobenzene to aniline.

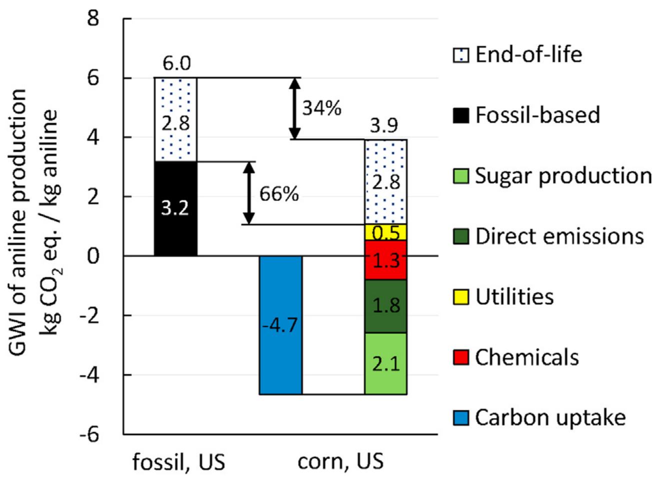

Fig. 4. Global warming impacts (GWI) of aniline production in the US, using either fossil feedstock or corn. Carbon uptake shows the amount of CO_2 sequestrated in the sugar. Sugar production includes all upstream activities of feedstock production (e.g., farming, transport, and processing) and any substitution credit for the by-products of feedstock production. Direct emissions are the direct emissions of the bio-based aniline process. Chemicals include emissions due to the production of ammonia, nitric acid, and hydrochloric acid. Utilities include the impact of steam, heat, cooling water, and wastewater treatment. End-of-life assumes the release of all carbon stored in aniline as CO_2, without energy recovery. (Individual numbers do not add up to the total due to rounding).

production contributes most to the non-biogenic emissions, with 54% (2.1 kg CO_2eq/kg aniline). The second-largest contribution is due to the production of sodium hydroxide, hydrochloric acid, and ammonia required in the process (34% = 1.3 kg CO_2eq/kg aniline). The remaining contribution to the global warming impact is caused by the utilities steam, electricity, water, and wastewater treatment (14% = 0.5 kg CO_2eq/kg aniline).

When stored carbon is not released at the end-of-life, bio-based aniline has a global warming impact of 1.0 kg CO_2eq/kg aniline compared to fossil-based aniline with 3.2 kg CO_2eq/kg aniline. In this case, bio-based aniline would reduce emissions by 66% compared to fossil-based production. This high reduction in GHG emissions is only achieved if the aniline is not combusted but stored at its end-of-life. The absolute reduction in GHG emissions is 2.1 kg CO_2eq/kg aniline and independent of assumptions regarding end-of-life.

When no substitution credit is given for any of the wet-milling by-products, bio-based aniline still has a lower global warming impact and abiotic depletion than fossil-based aniline. This scenario is discussed in more detail in the SI (Section S1).

4.1.2. Abiotic depletion potential-fossil

The abiotic depletion potential-fossil of 1 kg bio-based aniline is to 45.0 MJ from cradle-to-gate compared to 65.1 MJ per kg fossil-based aniline (Fig. 5). Thus, the utilization of biomass reduces the consumption of fossil energy by 31%. The relative contribution of the different activities is similar as for global warming: the largest share is due to feedstock production (44%), followed by the production of chemicals (42%) and utilities (14%).

4.1.3. Eutrophication and acidification potential

In contrast to global warming impacts and fossil depletion, the impacts in eutrophication and acidification increase for bio-based aniline compared to fossil-based aniline: Bio-based aniline has a cradle-to-gate acidification potential of 10.6 g SO_2eq/kg aniline and a eutrophication potential of 7.0 g PO_4^{3-}eq/kg aniline compared to 2.9 g SO_2eq and 1.7 g PO_4^{3-}eq/kg for fossil-based aniline (Fig. 5).

For both eutrophication and acidification potential of bio-based aniline, the largest contribution is feedstock production: 71% for acidification and 88% for eutrophication. Since the impacts in these categories depend strongly on the type of feedstock used, these categories are discussed in more detail with additional feedstock options below.

The production of chemicals also has a significant contribution to the acidification potential with a share of 22% but has a much smaller contribution to the eutrophication potential with a share of 7%. The larger contribution of chemicals to acidification is mainly due to the large acidification potential of sodium hydroxide production. The utilities have the smallest contribution to acidification and eutrophication with a share of 7% and 6%, respectively.

4.2. Sensitivity to location and feedstock

The preceding results for bio-based aniline from US corn showed that sugar production contributes most to all impact categories. Since the impact of sugar production depends strongly on the type of feedstock used, we also study alternative feedstocks. In this section, we discuss global warming impacts and eutrophication potential in detail, as the results for abiotic resource depletion and acidification are qualitatively similar (See Section S1 in SI for an in-depth discussion).

In the EU, fossil-based aniline production has lower global warming impacts than in the US with 5.1 kg CO_2eq compared to 6.0 kg CO_2eq from cradle-to-gate (Fig. 6). This difference is due to nitrous oxide emissions in background processes for nitric acid and benzene production. No data is available to us for fossil-based aniline production in Asia.

Bio-based aniline has a lower global warming impact than fossil-based aniline for all considered feedstocks. Furthermore, even when no substitution credit is given to any of the feedstocks, global warming impacts of bio-based production are still lower than fossil-based production (See Section S1 in SI).

Aniline produced from corn stover has the lowest global warming impacts, with cradle-to-grave emissions of 1.9 kg CO_2eq/kg aniline, a reduction of 69% compared to fossil-based aniline in the US. The impact is so low since corn stover was assumed as waste. After corn stover, sugar cane has the next lowest global warming impacts, with a cradle-to-grave impact of 2.6 kg CO_2eq/kg aniline. Aniline based on sugar beet and corn results in cradle-to-grave emissions of 3.5 and 3.9 kg CO_2eq/kg aniline, respectively.

From cradle-to-gate, the global warming impacts are negative for aniline based on corn stover or sugar cane with −0.9 and −0.2 kg CO_2 eq/kg aniline, respectively. Thus, bio-based aniline has the potential to become a carbon-negative technology if the end-of-life does not release carbon but leads to permanent storage. However, bio-based aniline should not be assumed as a carbon-negative technology by default.

Abiotic depletion potential of fossil-based aniline production in the US is slightly higher (65.1 MJ/kg) than for fossil-based aniline production in the EU (61.8 MJ/kg). The difference in fossil-based production between US and EU is far less pronounced in abiotic depletion than in global warming or eutrophication since the additional nitrous oxide emissions do not affect abiotic depletion. Bio-based aniline reduces abiotic depletion by 30.8–53.8%, depending on the feedstock. Corn-based aniline has the highest abiotic depletion potential with 45.0 MJ/kg, due to its high fertilizer demand for cultivation and energy use during processing into sugar. Corn-based aniline is followed by beet-based aniline with 34.4 MJ/kg. Corn stover and sugarcane-based aniline have the lowest abiotic depletion potential with 31.8 MJ/kg and 30.1 MJ/kg,

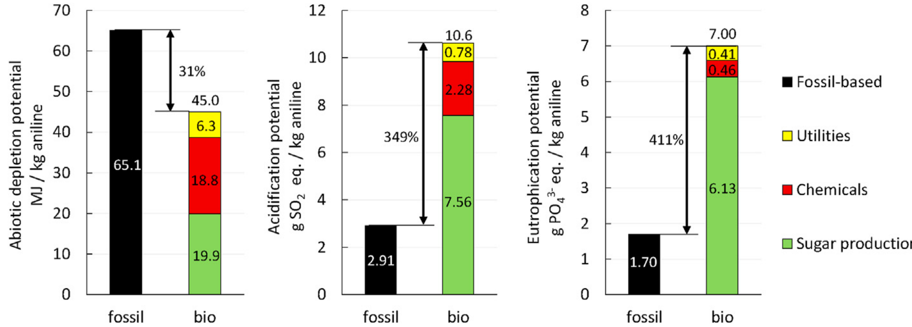

Fig. 5. Cradle-to-gate environmental impact of bio-based and fossil-based aniline in the impact categories abiotic depletion potential fossil, acidification and eutrophication potential.

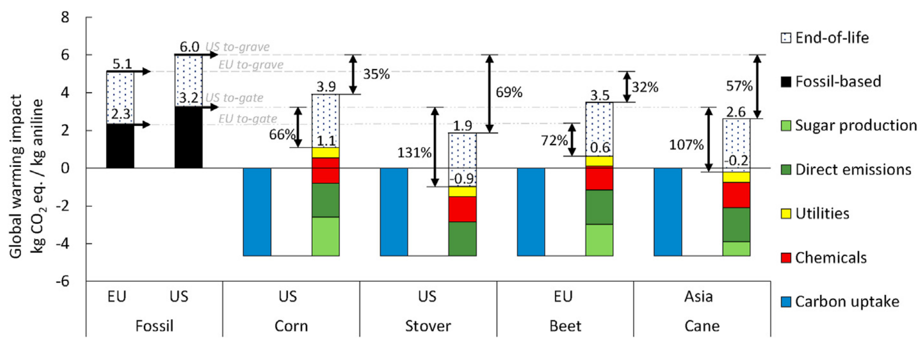

Fig. 6. Global warming impacts of fossil- and bio-based aniline production in the regions US, EU and Asia using the feedstocks corn, corn stover, sugar beet and sugar cane for the bio-based aniline production.

respectively.

Acidification potential for fossil-based aniline production in the US is slightly higher than in the EU with 2.9 g SO_2eq/kg compared to 2.3 g SO_2eq/kg. Bio-based aniline increases acidification potential for all investigated feedstocks by 231–441%. This increase can mainly be attributed to sugar production. For bio-based production, corn-based aniline has the highest acidification potential with 12.8 g SO_2eq/kg. Corn-based aniline is followed by beet-based aniline with an acidification potential of 8.2 g SO_2eq/kg. For both corn and beet-based aniline, acidification is mainly associated with the cultivation of biomass. Corn-stover-based aniline has an acidification potential of 7.9 g SO_2eq/kg. Acidification potential is high relative to other impacts of corn-stover-based aniline. In contrast to the other feedstocks, the high acidification potential of corn stover is not associated with cultivation emissions but mainly with the combustion of large amounts of lignin during sugar production. Sugar cane-based aniline has the lowest acidification potential with 6.7 g SO_2eq/kg.

The eutrophication potential of fossil-based aniline is higher in the US than in the EU due to higher nitrous oxide emissions: The eutrophication potential of 1 kg fossil-based aniline is 1.7 g PO_4^{3-}eq in the US and 0.7 g PO_4^{3-}eq in the EU. The eutrophication potential of bio-based aniline is dominated by the feedstock production for all feedstocks except corn stover, while all other activities only have a minor contribution. The feedstock with the highest eutrophication potential is sugar cane, with 14.0 g PO_4^{3-}eq/kg aniline. Compared to fossil-based aniline in the US, aniline based on sugar cane increases the eutrophication potential by more than a factor of 6. This high eutrophication potential is due to the excessive use of phosphate fertilizers during sugar cane cultivation in Thailand. The second highest eutrophication potential is already half the value for sugar cane and is aniline based on corn with 7.0 g PO_4^{3-}eq/kg aniline. Aniline based on sugar beet results in a eutrophication potential of 2.7 g PO_4^{3-}eq/kg aniline. This lower eutrophication potential of sugar beets is due to high substitution effects and not due to the inherently low eutrophication potential of sugar beet cultivation. When no credit for the substitution of barley by beet pulp is given, the eutrophication potential of sugar-beet-based aniline would nearly triple. Corn stover results in the lowest eutrophication potential at 1.2 g PO_4^{3-}eq/kg aniline and is the only feedstock that has a lower eutrophication potential than fossil-based aniline. Again, the low eutrophication potential assigned to the aniline is due to the assumption that corn stover is a waste product.

4.2.1. Indirect land-use change

The previous results for the global warming impacts did not include emissions due to land-use change. Here, we now consider the effect of land-use change on bio-based aniline production based on the broad range of values published in the literature (Fig. 7).

For corn, land-use change effects corn-based aniline production most, adding between 0.3 and 1.3 kg CO_2eq/kg aniline to the global warming impact of bio-based aniline production. However, global warming impacts for corn-based aniline are still 15–29% lower than for fossil-based aniline compared to 35% without land-use change. For corn stover, land-use change lowers the emissions slightly by 0.04–0.05 CO_2eq/kg aniline but does not change the global warming impacts significantly.

In the case of sugar beet, land-use change adds 0.2–0.7 CO_2eq/kg aniline to the global warming impacts, decreasing global warming impact reductions from 32% to 20–28%. Land-use change adds 0.6–0.8 CO_2eq/kg aniline for sugar cane, reducing global warming impacts by 44–46% compared to 57% without land-use

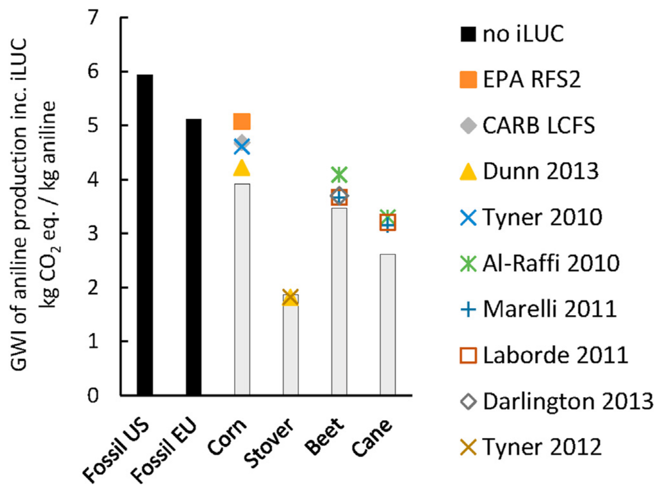

Fig. 7. Global warming impacts of fossil- and bio-based aniline production (black) where the symbols include indirect land-use change (iLUC) using values from different studies.

change. However, the land-use change results for sugar cane do not necessarily apply to Thai sugar cane cultivation and should thus be treated with care.

Nevertheless, while the inclusion of land-use change increases the global warming impact of bio-based aniline production, they remain lower than the global warming impacts of fossil-based aniline production for all feedstocks. This wide range of values used for indirect land-use change suggests that this result is robust. Importantly, all values of indirect land-use change mandated by government authorities, here EPA and California Resource Board, still result in a reduction of global warming impacts. However, land-use change should be monitored for any actual application. More detailed information is available in the SI Section S4.

4.3. Feedstock demand and availability

The extensive use of bio-based feedstocks could increase environmental impacts and has fueled concerns about food security, but could also stimulate job and economic growth in rural regions. To explore these varied impacts, we discuss the amount of feedstock required to fuel one large-scale aniline plant with a capacity of 100 kt/a and compare its demand to the feedstock available in each region. While this analysis is far from a complete assessment of the effects of large-scale bio-based aniline production on the agricultural system of a region, it can at least provide a sense of scale.

For the calculation of the available feedstock, the following countries are included in each region; US: the United States, EU: EU 27 plus the United Kingdom, Asia: China, India, and Thailand.

The countries in Asia are chosen to include the three largest regional producers of bio-ethanol. The data for feedstock production is taken from the USDA (Department of Agricu, 2018), Eurostat (European Comission and Euros, 2018), the RFA (2019) and the FAO (Food and Agriculture Orga, 2019) (Details in S3). All data are from 2018.

The operation of one 100 kt aniline plant requires about 0.1% of the annual corn harvest in the US, 1.7% of the annual sugar beet harvest in the EU, or 0.4% of the sugar cane yield in Asia. When the feedstock requirement of a 100 kt aniline plant is compared to the feedstock requirement of the already established ethanol production, the 100 kt plant would require 0.3%, 3.7%, or 2.9% of the feedstock currently used for US, EU or Asian bio-ethanol production, respectively. The larger relative feedstock requirement in the EU is primarily due to a rather small bio-ethanol industry in the EU as well as sugar-beets not being a crop with a high production volume. If the choice of feedstock in the EU is additionally expanded to include corn and wheat, only about 0.2% of the annual harvest of these three crops would be required for one 100 kt plant.

These findings show that the addition of a 100 kt bio-based aniline plant would only require a small fraction of the feedstock currently used for ethanol production in the EU or Asia and an even smaller fraction in the US. Satisfying the global aniline demand with bio-based aniline would require about 16.5% of the feedstock currently used for bio-ethanol production in the US.

5. Conclusions

The first pathways for the bio-based production of aromatic chemicals are emerging. In this study, we present the first prospective LCA of the aromatic chemical aniline produced from biomass based on simulation data for a production scale plant. Our results show that bio-based aniline could reduce the global warming impacts of aniline production by 35–69% from cradle-to-grave compared to fossil-based aniline.

In contrast to global warming impacts and abiotic depletion, eutrophication is increased by a factor of 2.9–7.2 for the production of bio-based aniline compared to fossil-based aniline when first-generation feedstocks are used. However, the utilization of second-generation feedstocks such as corn stover could reduce eutrophication of aniline production in the US by as much as 30% compared to fossil production, though the acidification potential remains high.

An analysis of feedstock availability reveals that the addition of one world-scale 100 kt bio-based aniline plant would be a much larger addition to the current bio-based production capacities in Asia and the EU than to the capacities in the US. Diverting 16.5% of the feedstock currently used for ethanol production in the US would be sufficient to supply the whole world with bio-based aniline.

In conclusion, our prospective LCA illustrates the great potential of bio-based aniline to reduce greenhouse gas emissions. This large potential warrants further research and development towards bio-based aniline as a potential contribution towards a chemical industry independent of fossil resources.

CRediT authorship contribution statement

Benedikt Winter: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Raoul Meys:** Methodology, Writing - review & editing. **André Bardow:** Conceptualization, Funding acquisition, Methodology, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The funding for this research project was provided by Covestro Deutschland AG. There are no further conicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2021.125818.

7. Supporting information

- SI-bio-based-aniline.dox: Includes additional data used for the Life Cycle Assessment
- background-processes.xlsx: Includes list of all background processes used

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