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ARTICLE TYPE

Hexamethylenediamine (HMDA) from Fossil vs. Bio-based Routes: an Economic and Life Cycle Assessment Comparative Study

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Hexamethylenediamine (HMDA) is one of the key intermediates in the preparation of nylon 6-6 by polycondensation with adipic acid. Currently, the most extended commercial process for HMDA manufacture proceeds via the hydrogenation of adiponitrile in ammonia, which is in turn produced by the hydrocyanation of butadiene. In this paper, we explore three alternative bio-based paths for HMDA production starting from high fructose syrup made from maize and potato-derived starch and using 5-hydroxymethylfurfural (HMF) as intermediate building block. The different routes have been compared using a combined economic and life-cycle assessment study including a sensitivity analysis on potential key parameters. Overall, our study reflects a higher economic benefit and a lower environmental impact of the benchmark fossil route. As for the environmental impact, the most advantageous of the three bio-based routes could present benefits in terms of CO₂ footprint when the carbon sink is taken into account, but at the expense of a higher impact in terrestrial, marine and freshwater eutrophication. Possible process improvements to make bio-based routes affordable for HMDA production are proposed as an attempt to draw general rules for process eco-design.

Introduction

The economy of developed and emerging countries hangs almost entirely on fossil raw materials, with more than 90% of organic chemicals issued from crude oil transformations.¹ Both the forecasted depletion of fossil resources and their strong contribution to climate change have triggered the development of innovative sustainable technologies capable of reducing oil dependency. Biomass represents a huge reservoir of renewable carbon that should provide in the forthcoming years a rich variety of platform molecules that could be further used as building blocks for the synthesis of chemicals.² In this context, it is urgent for the chemical industry to identify and develop renewable feedstocks offering efficient, harmless and environmentally friendly routes to commodities, fuels and specialty chemicals for building integrally sustainable solutions in a broad variety of markets and scenarios.³

This goal, which is compatible with a process eco-design strategy in line with the Anastas' Twelve Principles of Green Chemistry,⁴ imposes a critical and rigorous analysis of the main parameters and variables affecting bio-based processes and their boundaries. Key to this analysis is the identification of convenient raw materials and sourcing with a clear insight into their ecological footprint (*e.g.*, amount of water and energy used, type of fertilizers and pesticides, type of farming), the energy demand for concentrating, separating and processing the reagents from the raw materials, the yield of catalytic reactions, the possible hazards and risks, and the geographical location of the production site. Once any possible route has been identified, a sustainability assessment can be performed to unveil the effect and sensitivity of the most important parameters and variables on the capital and operation costs, as well as the environmental impact with regards to any possible fossil-based

benchmark. At this stage, it is essential to establish a tradeoff between the economic feasibility, environmental impacts, risks, and potential benefits associated to each option.⁵

The eco-design of greener pathways to commodities and specialty chemicals is a challenging task due to the limited information available on feedstocks and processes. As a result, it is sometimes difficult to draw a wide-ranging picture of potential benefits of bio-based processes compared to fossil-based benchmarks, leading to incomplete or even biased conclusions on their potential green credentials. For instance, serious concerns have been raised on the benefits of first and second-generation biofuels (*e.g.*, bioethanol) compared to fossil fuels for reducing greenhouse gas (GHG) emissions due to a narrow scope regarding the system boundaries and the allocation methods used for the attribution of environmental impacts.⁶ Indeed, the estimated GHG emissions from bioethanol can diverge from 32% higher to 20% lower compared to the use of gasoline due to N₂O and CO₂ emissions generated in other parts of the life cycle. Furthermore, despite a lower consumption of non-renewable resources and a reduction of GHG emissions,⁷ bioethanol and extensively other bio-based alcohols (*e.g.*, 1,3-propanediol) and acids issued from corn-derived glucose *via* fermentation are expected to intensify the strain on ecological goods and services due to the depletion of natural resources.⁸ Similar conclusions can be drawn for the manufacture of bioethanol-derived chemicals, such as ethylene glycol and ethylene for bio-PET and bio-PVC, respectively,⁹ and higher alcohols produced by the Guerbet reaction.¹⁰

In this paper, we concentrate our attention on potential bio-based paths for the synthesis of hexamethylenediamine (HMDA), one of the two key intermediates in the preparation of nylon 6-6 by polycondensation with adipic acid.¹¹ The HMDA world production in 2011 was 1.32 Mt with a projected average annual growth of 1.9%

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until 2020.¹² The most extended commercial process for HMDA manufacture is based on adiponitrile (ADN) hydrogenation in ammonia over a cobalt or iron catalyst (*e.g.*, Dupont process, Fig. 1).¹³ ADN is produced by the sequential hydrocyanation of butadiene (BD) obtained from the C4 cut using a Ni-tri-*o*-tolyl phosphite (NTOTP) catalyst. Overall, this process, labeled hereinafter as route 1 and serving as benchmark, can be expressed as follows

➤ **Route 1:** BD + HCN → ADN → HMDA

As an alternative, it would be highly desirable to conceive greener pathways affording HMDA with a lower number of steps and starting from bio-based reagents. The simplest approach for producing HMDA is by replacing petro-BD as raw material for a bio-based analogue produced using bioethanol,¹⁴ allowing the synthesis of bio-HMDA without additional capital costs. In such a case, 4 C atoms (BD) out of the 6 C atoms of HMDA would be issued from biomass. Patel and co-workers conducted a life cycle assessment (LCA) study on this process, pointing out a stronger economic constraint, a similar impact of the raw materials, and comparable GHG emissions for bio-based butadiene (bio-BD) compared to the conventional fossil-based benchmark.¹⁵ Nevertheless, alternative pathways might be foreseen for bio-HMDA production starting from molecules issued from biomass such as succinic acid,¹⁶ hexane,¹⁷ furfural,¹⁸ glycerol,¹⁹ levulinic acid,¹⁸ adipic acid,²⁰ lactic acid,²¹ and 5-hydroxymethyl furfural (HMF).²² Fig. S1 in the ESI shows a non-exhaustive panel for these speculative routes. However, to our knowledge, the techno-economical and environmental feasibility of all these paths has not yet been demonstrated.

Herein we explore the potentials of HMF as a building block for producing bio-HMDA given its facile access from carbohydrates *via* catalytic dehydration. To this aim, a comparative economic and LCA study has been performed on three potential yet unexplored bio-based routes starting from fructose (*i.e.* high fructose syrup, HFS) for HMF production and involving intermediates issued directly from HMF (*i.e.* DFF, THFDM and AM-THF, Fig. 2).²³ These processes, labeled here as routes 2-4, can be summarized as follows:

➤ **Route 2:** HMF → THFDM → 1,6-HDO → HMDA

➤ **Route 3:** HMF → THFDM → AM-THF → HMDA

➤ **Route 4:** HMF → DFF → AM-THF → HMDA

Our choice has been partially motivated by a recent study from Rennovia pointing out the direct manufacture of bio-HMDA from HFS at a production cost 20-25% below than that of conventional petro-HMDA and with comparatively lower capital costs.²⁴ Additional projected benefits include a 50% reduction of GHG emissions compared to petro-HMDA.

Noteworthy, even if the industrial development of routes 2-4 towards HMDA has not been realized yet, these pathways seem feasible according to the present state of the art. This study is intended to address the main economic and environmental barriers of alternative bio-based processes towards bio-HMDA manufacture as an attempt to draw general rules for *eco-design* under a reasonable set of simplifying assumptions on allocation methods and using a reduced yet comprehensive set of available information. We also assess the robustness of the environmental outcome given the uncertainty of the input information. In practice, the processes for routes 2-4 were simulated relying on data available from patents on fructose issued from maize and potato starch as starting material. The environmental impact of the different routes was assessed using a Life Cycle Assessment (LCA). This methodology has been widely

used by both academic and governmental institutes, and has also been adopted and promoted by international companies such as Solvay.

Methodology

Our combined economic and LCA study can be divided into 5 steps:²⁵ (i) Scope and Functional Unit Definition, (ii) Inventory Analysis, (iii) Life Cycle Impact Assessment (LCIA), (iv) cost assessment, and (v) interpretation. The inventory analysis and impact assessment stages were carried out using SimaPro 7.3.3 software provided with the Ecoinvent v2.2 database,²⁶ whereas the unit costs of raw materials were obtained from the references indicated in Table 1.

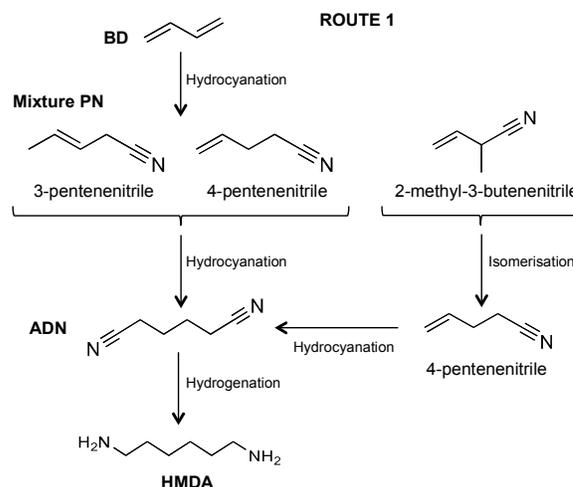


Fig. 1. Dupont process for HMDA manufacture *via* BD hydrocyanation (Route 1 or benchmark). Image adapted from ref.¹¹

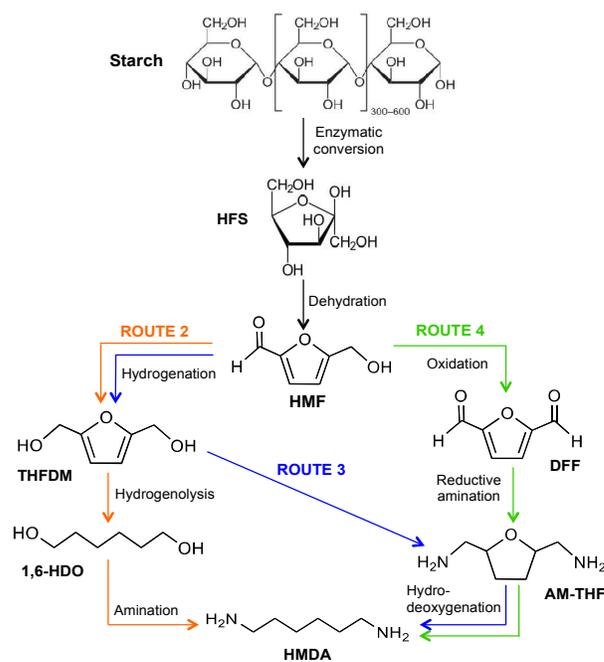


Fig. 2. Potential routes towards bio-HMDA using platform molecules issued from biomass (Routes 2-4). These routes correspond to processes either available in the literature or affordable according to the present state-of-the-art.

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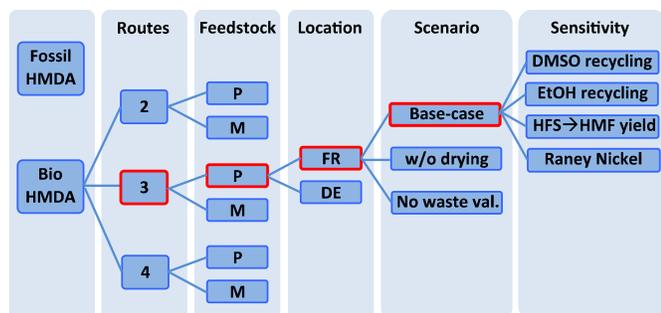


Fig. 3. LCA scope for HMDA production via the fossil-based route 1 and three alternative bio-based routes 2-4. In red, route 3P FR. Nomenclature: M, grain maize; P, potatoes; FR, France; DE, Germany.

Table 1. Main variables contributing to the cost and environmental footprint of the different routes for HMDA manufacture. The ‘Best Case’ and ‘Worst Case’ columns indicate the minimum and maximum expectable values, respectively. The ‘Base Case’ refers to the values retained for the process inventory (Tables S1, S2).

Variables for routes 1-4		Best Case	Base Case	Worst Case	Ref.
Economics	Butadiene, €/kg	0.30	1.15	2.60	(a)
	Natural gas, €/kg	0.015	0.027	0.040	(b)
	Ammonia, €/kg	0.185	0.455	0.540	(c)
	HFS42%, €/kg	0.22	0.49	0.49	(d)
	Hydrogen Iodide (HI), €/kg	22.37	42.65	42.65	(e)
LCA + Economics	HMF catalyst, g/kg	0.1	1.54	10.0	(f)
	Raney nickel catalyst, g/kg	0.1	1.0	5.0	(f)
	Pd/SiO ₂ catalyst, g/kg	0.1	0.1	1.0	(f)
	DMSO recycling rate, %	99.9	99.9	98.0	(f)
	Ethanol recycling rate, %	99.9	99.9	98.0	(f)
	HI recycling rate, %	99.9	99.9	98.0	(f)
	HFS → HMF yield, %	87.7	83.5	49.3	(g)
	Waste valorization	Yes	Yes	No	(h)
	Complete HFS drying	No	Yes	Yes	(i)

Refs: (a) Butadiene Europe Spot fob, Q1/2005-Q1/2013 (ref.²⁷); (b) Trading natural gas 2011-2013 (ref.²⁸); (c) Ammonia Europe Spot cfr, Q1/2005-Q1/2013 (ref.²⁷); (d) Milling & Baking News, US Midwest spot price HFCS42% Q1/2005-Q1/2013 (ref.²⁹); (e) Average HI cif price 2008-2012 (ref.³⁰); (f) process assumption, (g) according to Table S4 (ESI), (h) “yes”: on site valorization of organic wastes by combustion in a boiler for steam generation (steam credit); “no”: wastes burned outside, (i) “yes”: HFS was dried completely for HMF synthesis; “no”: HFS at 72.5% w/w dry matter was not dried before HMF manufacturing.

Our methodology is not restricted to the CO₂ footprint, which has been frequently presented in the past as the sole environmental indicator for assessing the attractiveness of biomass-derived chemicals. Instead, a wider panel of indicators was here adopted to account for pollution transfer between the different impact categories in the three main areas of protection: health, ecosystem quality, and resource depletion.

LCA Scope and Functional Unit Definition

The scope of this study is a comparative LCA between the above

stated routes for producing HMDA (Fig. 3): one commercial fossil-based route considered here as benchmark (route 1), and three hypothetical bio-based alternatives using grain maize and potatoes as feedstock (routes 2-4). For the sake of clarity, the letters ‘M’ and ‘P’ have been used in combination with the route number to account for the feedstock (e.g., 2M means route 2 starting from grain maize). The functional unit used as basis for comparison was defined as 1 kg of HMDA.

HMDA manufacture from the different feedstocks was assessed from cradle-to-gate (“gate” here stands for the outlet of the HMDA manufacturing factory). Accordingly, the system boundary comprised not only the processes directly involved in HMDA production (the foreground system), but also secondary processes (background system) such as the manufacture of the raw materials and the generation of electricity, for which existing databases were used.²⁶

Location and Supply Chain

Two manufacturing locations for HMDA were considered (Fig. 3), *i.e.* France (FR) and Germany (DE), since both countries are major maize and potato starch producers. We assumed that the process used for starch production was similar enough between both countries to use the same Ecoinvent LCI database relying on German data (maize starch at plant/DE, and Potato starch at plant/DE, respectively). The sole difference between both locations was that the original electricity mix (medium voltage at grid/DE) was substituted by medium voltage at grid/FR for France. The same strategy was adopted in the four routes: all mass and energy balances were kept identical between the German and French locations, but using the corresponding electricity mix. The underlying idea behind this approach was to obtain a geographically dependent environmental analysis for HMDA manufacture.

Life Cycle Inventory Analysis (LCIA)

Table 1 lists the most relevant variables contributing to the environmental footprint of the different routes for HMDA production. In this table, the ‘Best Case’ and ‘Worst Case’ columns indicate, respectively, the minimum and maximum likely values for each variable to be further used in the sensitivity analysis, whereas the ‘Base Case’ columns refers to the values retained for the inventory (Table S1 in ESI). The physical properties of the molecules involved in the calculations are listed in Table S5 in ESI. The catalysts and HI used for routes 3 and 4 were not registered in the Ecoinvent database. As these products are only present in very small quantities (0.5 wt.% of the raw material for route 1 and <0.2 wt% for routes 2-4), we decided not to take them into account in our analysis except for Raney nickel (A₁₄ in Table S1), for which the estimations were made relying on internal data.

Fossil-based route. Since no existing LCIA data set on fossil-based HMDA (route 1) is available in the Ecoinvent v2.2 database, a model process was built relying on mass and energy balances derived from the IHS PEP yearbook 2012 (Table S1).³¹ The corresponding flowsheet diagram with a clear definition of the boundaries is depicted in Fig. S2. Additional technical details are provided in the ESI.

Bio-based routes. Mass and energy balances were performed for the three bio-based paths to build the inventory in Table S1. The corresponding flowsheet diagrams are depicted in Figs. S3-S6. Note that all the catalyst consumptions rely on assumptions according to available data in the open and patent literature. For organic wastes, we assumed that steam could be generated by on-site waste burning in a boiler (steam credit in Table 1 & Table S1). Furthermore, we assumed that the different reaction intermediates could be isolated with 100% yield and 100% purity. The bio-based paths can be divided into three main steps, two of which are common and one is particular to each case:

Starch → *HFS* (enzymatic conversion of starch into HFS)

The three bio-based paths start with the conversion of starch into HFS. The environmental footprint attributed to the manufacture of HFS from starch could not be found in public databases. Therefore, a model was built to assess the environmental impacts relying on available enzymatic processes as described in the ESI. Two different types of starch were considered being obtained from maize and potato. The data for both types of starch are available in the Ecoinvent LCI database relying on the study of Würdinger et al.,³² who made an inventory of maize- and potato-starch processes common in Germany:

- Transport of the maize grains with 14 wt.% water content to the starch plant (distance 100 km). The final product (starch) has a water content of 14 wt.%.
- Transport of potatoes with a 25 wt.% dry-matter content to the starch plant (distance 25 km). The final product (starch) has a water content of 20 wt.%.

In our calculations, we assumed that starch is diluted up to 35 wt.% in water before being transformed into HFS, which is a typical concentration for a saccharification process. Table S2 in the ESI shows the inventory of HFS from starch.

HFS → *HMF* (dehydration of HFS into HMF)

The next step, which is also common to the three bio-based paths, entails the conversion of HFS into HMF. Although this step could theoretically occur in aqueous medium, the current state-of-the-art describes the use of DMSO as solvent for HMF production at moderate-to-high yields. The base case assumes therefore that HFS must be completely dried before transformation into HMF in DMSO. Relying on current industrial knowledge, we assume that this drying step is performed using high-pressure steam.³³ A sensitivity study was performed in which HFS drying was excluded to simulate a theoretical case where the HMF reaction occurred in aqueous medium. More details on the reaction conditions and yields considered for further calculations are described in the ESI.

HMF → *HMDA* (hydrogenation/amination of HMF into HMDA, routes 2-4)

Fig. 2 displays three possible paths for the synthesis of HMDA from HMF. The LCI for the different routes was based on the mass and energy balances as detailed in the ESI. Fossil- and bio-based organic wastes (such as non-recycled DMSO solvent or by-products such as humins) were assumed to be *in situ* incinerated and the resulting energy to be valorized as steam for the base case scenario. The resulting CO₂ emissions were taken into account separately as fossil and biogenic CO₂ emissions.

Life Cycle Impact (LCI) Methods

Midpoint Impact Categories. The environmental impact of the fossil- and bio-based HMDA was assessed using the following 9 midpoint impact categories:

1. Climate change: Global Warming Potential over a time horizon of 100 years (kg CO₂ eq).
2. Ozone depletion: Ozone Depletion Potential (ODP) over a time horizon of 100 years (kg CFC-11 eq).
3. Particulate matter: quantified as PM_{2.5} (kg PM_{2.5} eq).
4. Photochemical ozone formation (kg NMVOC eq).
5. Acidification: Accumulated Exceedance (AE) (mole H⁺ eq).
6. Terrestrial eutrophication: Accumulated Exceedance (AE) (mole N eq).
7. Freshwater eutrophication: phosphorus considered as limiting factor in freshwater (kg P eq).
8. Marine eutrophication: nitrogen considered as limiting factor in marine water (kg N eq).
9. MJ primary non-renewable energy (MJ primary).

The first eight impact categories were derived from the ILCD 2011 method, whereas the last one was derived from the IMPACT 2002+ method. This multi-criteria panel of categories was selected to estimate the damage in the three main areas of protection: health, ecosystem quality, and resource depletion. It is worth noting that no impact category related to land use, deforestation and water resource depletion was used due to the poor quality of inventories in most of the background data available.

The category 'Climate Change' was divided itself into two sub-categories either including (w) or excluding (w/o) the 'carbon-sink' referring to the amount of bio-sourced carbon stored in HMDA. The corresponding amount of CO₂ was deducted from the Climate Change impact for all bio-based paths with no fossil-sourced carbon. The calculation of the carbon-sink (in kg eq CO₂/kg HMDA) was carried out as follows:

$$\text{Carbon-sink} = \frac{\text{mole bioC}}{\text{mole HMDA}} \times \frac{M_{w,\text{CO}_2}}{M_{w,\text{HMDA}}} = 6 \times \frac{44}{116} = 2.3 \quad (1)$$

Impact Score Breakdown. To better assess the origin of the environmental impact, a breakdown of the components for each route was given for each impact category:

1. Fossil CO₂: CO₂ emissions from the incineration of fossil-sourced waste (e.g., adipic acid, DMSO).
2. Electricity: electricity consumption.
3. Natural gas: for HCN synthesis (route 1) or for heat generation (all routes).
4. Chemicals: production of chemicals existing in LCI databases (e.g., BD, sulfuric acid).
5. Steam (drying): steam used for HFS drying.
6. Steam: all other uses of steam (e.g., distillation).
7. Cultivation/starch: cultivation of maize and potatoes, as well as starch production.
8. Waste treatment: incineration of fossil- or bio-based organic waste, such as lost non-recycled DMSO, but without taking into account CO₂ emissions.

Production scenarios. For each impact category, a dedicated study was performed to assess the influence of the different production scenarios on the output environmental footprint (three last rows in Table 1) while keeping the process variables constant at base case values. The following scenarios were considered using the values in the 'Best', 'Worst' and 'Base Case' columns in Table 1:

1. Base case: all standard values in 'base case' column.
2. w/o HFS drying: no HFS drying. Note that HFS drying is mandatory for our simulations (HMF produced using DMSO as solvent). Since there is no data are to support the feasibility of

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manufacturing HMF without previously drying the HFS syrup, the 'w/o HFS drying' case should be regarded as hypothetical.

- No waste valorization: no energetic valorization of waste by heat recovery.

Sensitivity analysis. For each impact category, a sensitivity analysis was performed using the so-called 'one-at-a-time-approach' to assess the influence of the input process variables on the output environmental footprint. In this analysis, the individual input variables were changed one at a time, while the remaining variables were held constant. This approach is simple, but it can overlook potentially sensitive variables. Furthermore, it does not take into account any possible interaction effects between the process variables. The following cases were considered using the values in the 'Best', 'Worst' and 'Base Case' columns in Table 1:

- DMSO 98%: worst case value for DMSO recycling rate (98%).
- EtOH 98%: worst case value for EtOH recycling rate (98%).
- HFS best: best case value for HFS → HMF yield (87.7%).
- HFS worst: worst case value for HFS → HMF yield (49.3%).
- Raney nickel high: high catalyst loss (worst case, 5 g/kg HMDA) for Raney nickel catalyst.
- Raney nickel low: low catalyst loss (best case, 0.1 g/kg HMDA) for Raney nickel catalyst.

Uncertainty analysis. An uncertainty analysis was carried out using the Monte Carlo (MC) tool available in the SimaPro 7.3.3 software. In this analysis, the uncertainty associated to the inventory data in the Ecoinvent v2.2 database was expressed directly on each midpoint impact category. For the bio-based 3P FR path, 63% of the inventory data incorporated uncertainty data (almost exclusively log-normal distribution), whereas this figure was 72% for the 1 FR route. In all the calculations for the foreground data, the same method was used as for the background data already present in the Ecoinvent database. This was done using a simplified approach based on the pedigree matrix.³⁴ The 95% confidence intervals of the estimated values were calculated based on square of geometric standard deviations, σ_g^2 , using the expression

$$\sigma_g^2 = \exp \left[\sum_{i=1}^6 \left[\ln(U_i)^2 \right] + \left[\ln(U_b)^2 \right] \right] \quad (2)$$

where U_1, U_2, U_3, U_4, U_5 and U_6 are the uncertainty factors of reliability, completeness, temporal correlation, geographical correlation, technological correlation, and sample size, respectively, and U_b is the basic uncertainty factor.

The latter factor is based on expert judgment and depends on the input (thermal energy, chemical product, transport, etc.). Each criterion receives a score of 1 up to 5 corresponding to five quality levels for which an uncertainty factor is attributed. The description of the quality levels and corresponding uncertainty factors for the foreground data can be found in Table S6. The uncertainty factor of sample size (U_6) exists in previous versions of the pedigree matrix, but is currently considered as an obsolete indicator. Accordingly, this factor was not taken into account in our calculations. The scores used for the pedigree matrix for the different steps of HMDA routes

1FR and 3P FR can be found in Table S7.

A statistical test was carried out for each impact factor to assess any statistically significant difference between the processes. In each analysis, SimaPro accounts for any shared uncertainty (e.g., electricity, chemicals, transport) by taking the same MC sampling sets. The test was performed by counting the number of MC runs in which the bio-based path showed a higher/lower impact than the fossil-based path for each impact category. In our calculations, we assumed that if at least 90% of the runs are favorable for one path, then the difference might be significant. To obtain representative results, 5,000 MC runs were executed in each simulation.

Assessment of production costs

We assumed that the HMDA production line might be operational for 8000 h/year with a capacity of 165 kt HMDA/year. The full manufacturing cost (FMC) of HMDA and its intermediates was calculated *ex-works* (i.e. without tax and transport) using the following expression

$$\text{FMC}(\text{€}/\text{kg}) = \frac{\text{Variable Cost} + \text{Fixed Cost} + \text{Depreciation}}{\text{Quantity produced}} \quad (3)$$

The fixed cost includes maintenance and labor costs, which were estimated using an internal Solvay method, as well as the depreciation of the facilities. Depreciation refers to the amortization cost of the industrial facility during its life in service. The variable cost was calculated using the expression

$$\text{Variable Cost}(\text{€}/\text{kg}) = \sum_{i=1}^n (A_i \times \text{Price}_{A_i}) \quad (4)$$

where A_i refers to all the items contributing to the inventory (Table S1), i.e. the raw material, catalysts, utilities, wastes and by-products, all expressed in their respective units (ex: kg, kWh, m³) per kg HMDA or kg intermediate. Table 1 lists the most relevant variables with 'min' and 'max' values used in the sensitivity analysis, whereas the 'base' values were retained for the inventory.

A series of miscellaneous chemicals were not considered in the inventory, since their quantities were too small and/or their prices too low. Furthermore, for the bio-based routes, water consumption and wastewater treatment were not taken into account, since they are not regarded to affect significantly the final cost. The cost ascribed to catalysts was estimated directly from the market price for precious metals as the metallic part of the catalyst bears most of the catalyst price for the different formulations.

The cost assessment was performed using prices of the first quarter of 2013. Such an approach provides a snapshot of the attractiveness of a process in real time without the disturbance of prices evolution. However, the price of some raw materials may fluctuate with time and affect accordingly the FMC of the products. Fig. S7 in the ESI illustrates this fluctuation for the two main raw materials considered in the cost estimation: BD and HFCS42%. Even if HMDA manufacture is located in Europe (i.e. France and Germany), a HFS supply from Europe does not seem a relevant choice. Currently, the European sugar quota system limits the HFS production to 5% of the total EU quota, limiting effectively its manufacture and increasing its price. However, by 2017, this limit is expected to be lifted,

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opening the market.³⁵ This means that the HFS price in EU would be probably similar to that in USA. Fig. S7 also shows that the US HFCS42% price increases rather smoothly and looks much more predictable than that of BD. This increase is driven by the high demand of ethanol, which has lifted the corn price. Accordingly, the US HFCS42% market price of Q1 2013 (0.49 €/kg) and the European Q1 2013 BD price (1.15 €/kg) were chosen as the base-case for our calculations.

The aforementioned methodology gives predictions of the full manufacturing cost with an error about $\pm 10\%$, but relies strongly on a careful assessment of prices and process assumptions. This accuracy level is based on predictive costing compared to industrial realizations. Note also that, since no significant difference in terms of FMC was found between the French and German locations, we focused our economic analysis solely on the former one.

Results

Production cost

Table 2 summarizes the estimated FMC for HMDA production from petro-BD (route 1) and from HFCS42% (routes 2-4) using Q1 2013 base-case prices and the inventories listed in Table 1. The estimated petro-based HMDA cost is 1.84 €/kg, which is cheaper than the cost estimated for the routes 3 and 4 at the best cases (ca. 2.15 €/kg). As the BD and HFS market prices fluctuate over time, Fig. 4 compares the different routes as a function of the HFCS42% and BD prices. The intersection of the horizontal and vertical dashed lines represents the situation corresponding to base-case prices (BD at 1.15 €/kg and HFCS42% at 0.49 €/kg). In contrast, for a HFCS 42% price at 0.49 €/kg, the cost advantage of the BD route would disappear if the BD price is higher than ~ 1.8 €/kg. If the BD price remains constant at 1.15 €/kg, then the HFCS42% price should be lower than ~ 0.3 €/kg for routes 3 and 4 to become cheaper. On the guidance of the historical and market data, both a BD price higher than 1.8 €/kg and a HFCS42% price lower than 0.3 €/kg are unlikely to occur. In light of these results, HMDA manufacture from BD hydrocyanation appears more economically advantageous provided that the assumptions indicated in Table 1 apply.

Fig. 5 explores the effect of the most contributive variables in the FMC of HMDA according to the variability indicated in Table 1. For route 1 (Fig. 5A), the key driver for the FMC is the BD price. This cost evolves from a minimum value of 1.1 €/kg to a maximum value of 2.9 €/kg if the three most influential costs (BD, ammonia, natural gas) are kept each at minimum and maximum values.

Fig. 5B provides a sensitivity analysis of the FMC of HMDA for the bio-based route 3. The HFS price is a main driver of the cost, as well as the HFS \rightarrow HMF yield, the catalyst consumption for HMF conversion, and the HI consumption during AM-THF conversion into HMDA. The estimated FMC of HMDA evolves from a minimum value of 1.2 €/kg to a maximum value of 7.0 €/kg. This sensitivity analysis shows that HMDA from HFS routes could compete with the fossil-based benchmark, but only under a scenario conditioned by either high BD and natural gas prices (or at least high peak prices for BD in very volatile scenarios), or reduced HFS prices.

Environmental analysis

Impact factor assessment results. Fig. 6 shows the main trends obtained for GHG emissions (midpoint impact category 1, w/o carbon-sink) for the aforementioned routes (base-case) as a function of the feedstock (maize grain and potatoes) and the location site (France and Germany). All bio-based paths display an apparent higher environmental impact than that of fossil-based route 1. The GHG emissions for the bio-based paths show values in the range

6.0-8.1 kg CO₂ eq / kg HMDA and 7.5-9.9 kg CO₂ eq / kg HMDA for the French and German locations, respectively. These values are higher than those estimated for route 1, showing GHG emissions of 5.5 and 5.8 kg CO₂ eq / kg HMDA, respectively. However, if the amount of bio-sourced carbon stored in HMDA (i.e. the carbon-sink, 2.3 kg CO₂ eq / kg HMDA) is taken explicitly into account, the estimated GHG emissions can be reduced to 3.8 kg CO₂ eq / kg HMDA for route 3P FR.

Table 2. FMC for HMDA manufacture for routes 1-4.

Route	1	2	3	4
FMC, €/kg HMDA	1.84	2.55	2.17	2.13

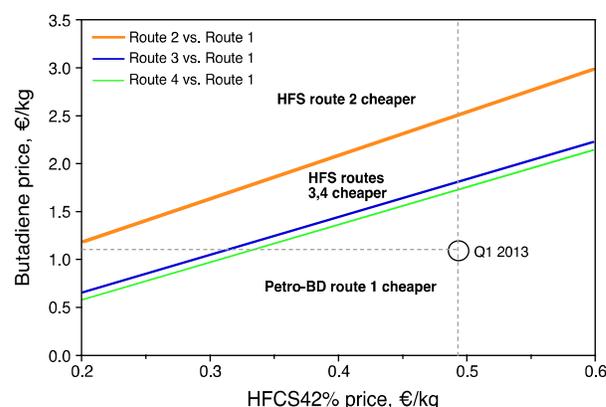


Fig. 4. Isocost curves for HMDA manufacture from bio-based routes 2, 3 and 4 compared to petro-BD route 1 as a function of the BD and HFCS42% prices for a production located in France.

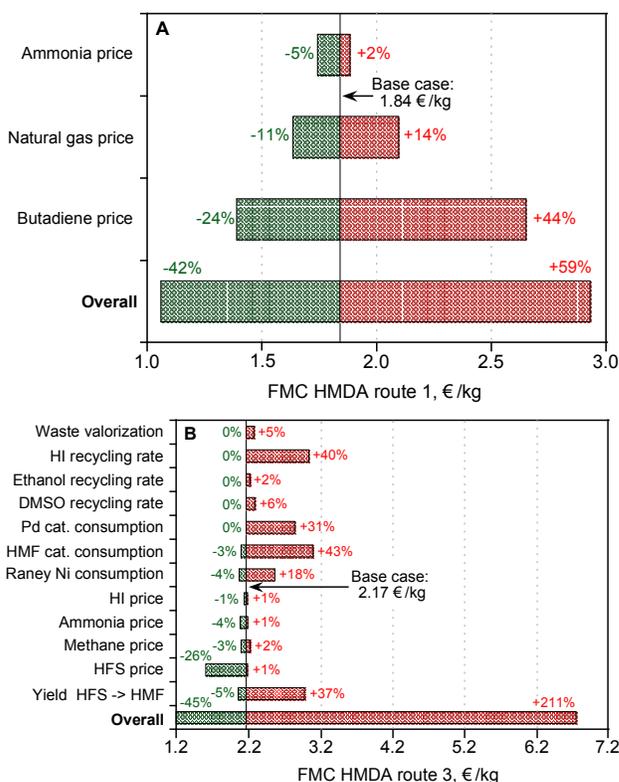


Fig. 5. Effect of the variability of the main process variables influencing the FMC of HMDA for the fossil-based route 1 (A) and the bio-based route 3 (B).

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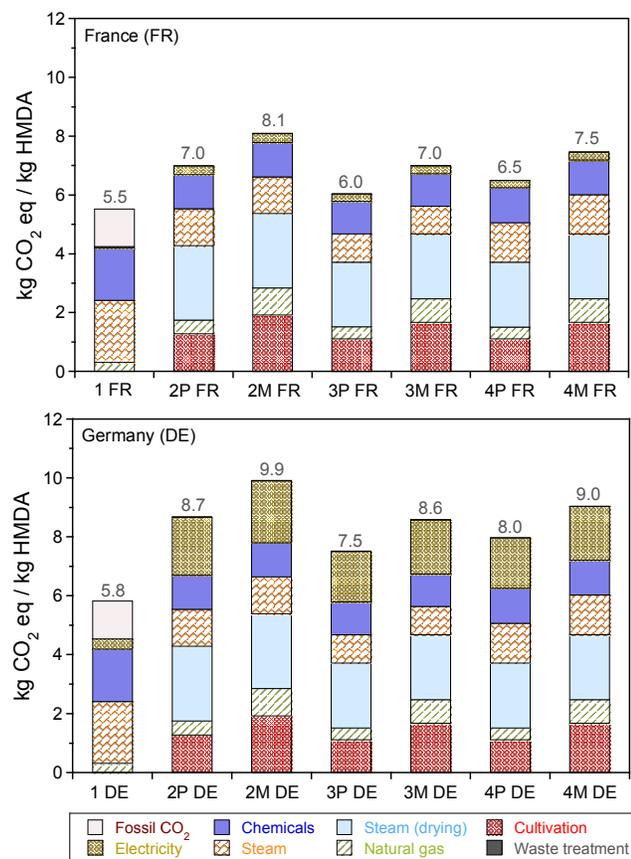


Fig. 6. Impact score breakdown for climate change (midpoint category 1 w/o carbon sink) for base-case HMDA manufacture in France and Germany. Nomenclature: FR = France, DE = Germany, M = Maize, 1-4 stands for the fossil route (1) and bio-based routes (2-4) as detailed in the Introduction.

The environmental impact of bio-based paths becomes more pronounced when maize is considered as feedstock instead of potatoes. This observation can be attributed, at least partially, to the lower crop yields achieved in maize cultivation. Finally, the German electricity mix has an overall negative effect compared to the French electricity mix due to the preponderant use of coal as energy source in Germany compared to 'greener' nuclear energy in France. Similar trends can be drawn for the other eight midpoint impact categories. The results are collected in Fig. 7 for terrestrial, marine and freshwater eutrophication (midpoint impact categories 7 and 8, respectively), and in Figs. S8-S13 in the ESI for the remaining categories. The breakdown of the impact scores shows that the two main contributors to the higher scores of bio-based paths are: (1) the feedstock cultivation (i.e. fertilizers used for maize and potato cultivation and the processes involved in their production), and (2) the steam used for HFS drying (i.e. fossil fuels required for steam generation). Terrestrial, marine and freshwater eutrophication are the three categories for which the three bio-based paths have a much

higher impact than that estimated for route 1, especially when using maize as feedstock. The two most common nutrients driving aquatic eutrophication are nitrogen and phosphorus, which are present in the fertilizers used for cultivation.

Sensitivity analysis. Given the important contribution of feedstock cultivation and the steam used for HFS drying, we decided to perform a sensitivity analysis to evaluate the effect of the HFS → HMF yield (which indirectly impacts the feedstock consumption) and the HFS drying on the final impact scores. Other process variables such as waste valorization, solvent recycling and catalyst consumption were also subjected to a sensitivity study. In these analyses, the best, base and worst cases were chosen for each of the selected variables (see Table 1).

Among the bio-based paths reported so far, route 3 using the French electricity mix and potatoes as feedstock (i.e. route 3P FR) provides overall the best results for all impact categories. We attribute this observation on the one hand to a lower HFS consumption per kg HMDA produced for route 3P FR compared to 2. On the other hand, route 3P FR entails a lower steam consumption compared to 4.

In light of the greener credentials offered by route 3P FR, we carried out a detailed sensitivity study on this path to evaluate the relative contribution of the different variables on the environmental footprint. Figs. 8 and 9 and Figs. S14-S17 in the ESI summarize the main results obtained. In the following lines, we will concentrate our attention on the climate change and three eutrophication categories (i.e. terrestrial, marine and freshwater). As expected, the HFS → HMF yield is a sensitive variable for the above stated impact categories. As a matter of fact, a yield variation from 49.3% to 87.7% for the worst- and best case results in 8.6 and 5.7 kg CO₂ eq / kg HMDA respectively, which is mainly attributed to the higher steam consumption for HFS drying. For marine eutrophication this yield variation corresponds to 0.052 and 0.028 kg N eq / kg HMDA respectively, which is almost entirely ascribed to a higher feedstock consumption and thus the use of fertilizers.

The scenario without HFS drying leads to a prominent reduction of steam consumption and in turn to a significant decrease (about 20%) on the climate change value. In contrast, no significant change is observed for the three eutrophication categories. The scenario without waste valorization leads to a higher steam consumption with a similar impact on the climate change and eutrophication categories, but to a lesser extent compared to the HFS → HMF yield and HFS drying step. The Raney nickel consumption exerts a significant impact on the categories particulate matter, acidification and freshwater eutrophication, which is mainly ascribed to the environmental impact of nickel mining. However, the impact scores of the best case (low catalyst loss) are only slightly below those of the base-case scenario. Finally, the DMSO and ethanol recycling rates exert a limited effect for all categories in the range of values listed in Table 1.

Overall, among the different scenarios selected, only the HFS → HMF yield and w/o HFS drying lead to similar or lower impact scores for the route 3P FR compared to 1 FR. This observation holds for the following categories: climate change, ozone depletion, particulate matter and non-renewable energy. For the remaining impact categories, especially terrestrial, marine and freshwater

eutrophication, regardless of the scenario selected, the 3P FR route is clearly unfavorable compared to 1 FR.

Uncertainty analysis

An uncertainty analysis was carried out to assess the statistical robustness of our simulations and in turn the validity of the comparisons between routes 3P FR and 1FR. Relying on the results

obtained in the sensitivity study, three scenarios for route 3P FR were assessed: (1) Base case, (2) HFS \rightarrow HMF yield (high), and (3) w/o HFS drying. In this analysis, we focused on the impact categories for which the above scenarios have a potential benefit compared to 1 FR: climate change, ozone depletion, particulate matter, and non-renewable energy.

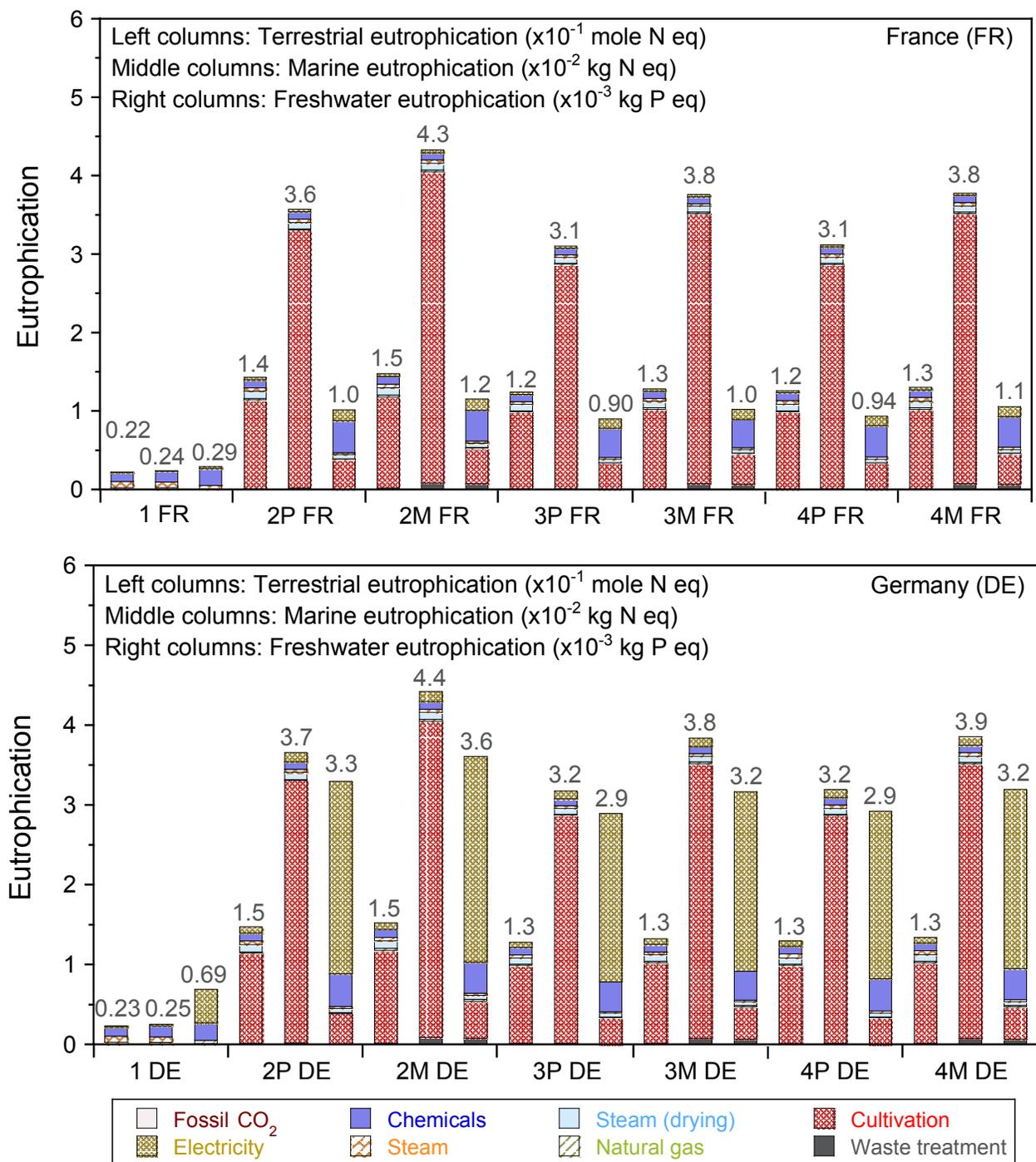


Fig. 7. Impact score breakdown for terrestrial, marine and freshwater eutrophication (midpoint categories 6-8) for base-case HMDA manufacture in France and Germany. Nomenclature: FR = France, DE = Germany, M = Maize, 1-4 stands for the fossil route (1) and bio-based routes (2-4) as detailed in the Introduction.

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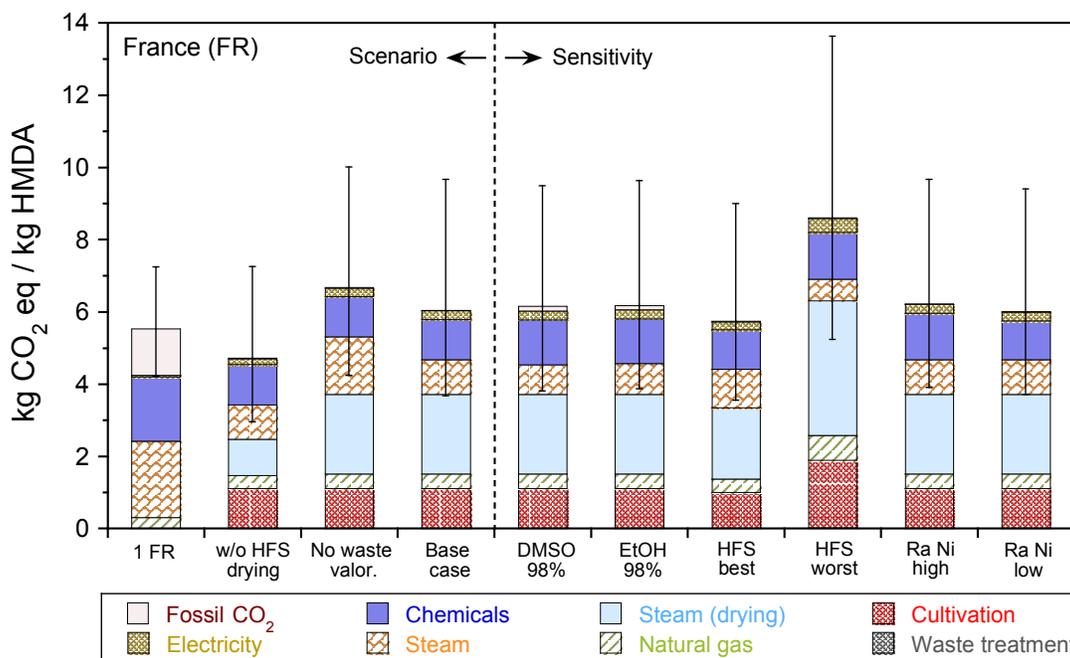


Fig. 8. Influence of HMDA production scenarios (left) and process variables (right) on climate change (midpoint category 1) for bio-based route 3P FR vs. 1 FR. The error bars (for a 95% confidence interval) were estimated with the SimaPro software using Monte Carlo simulations.

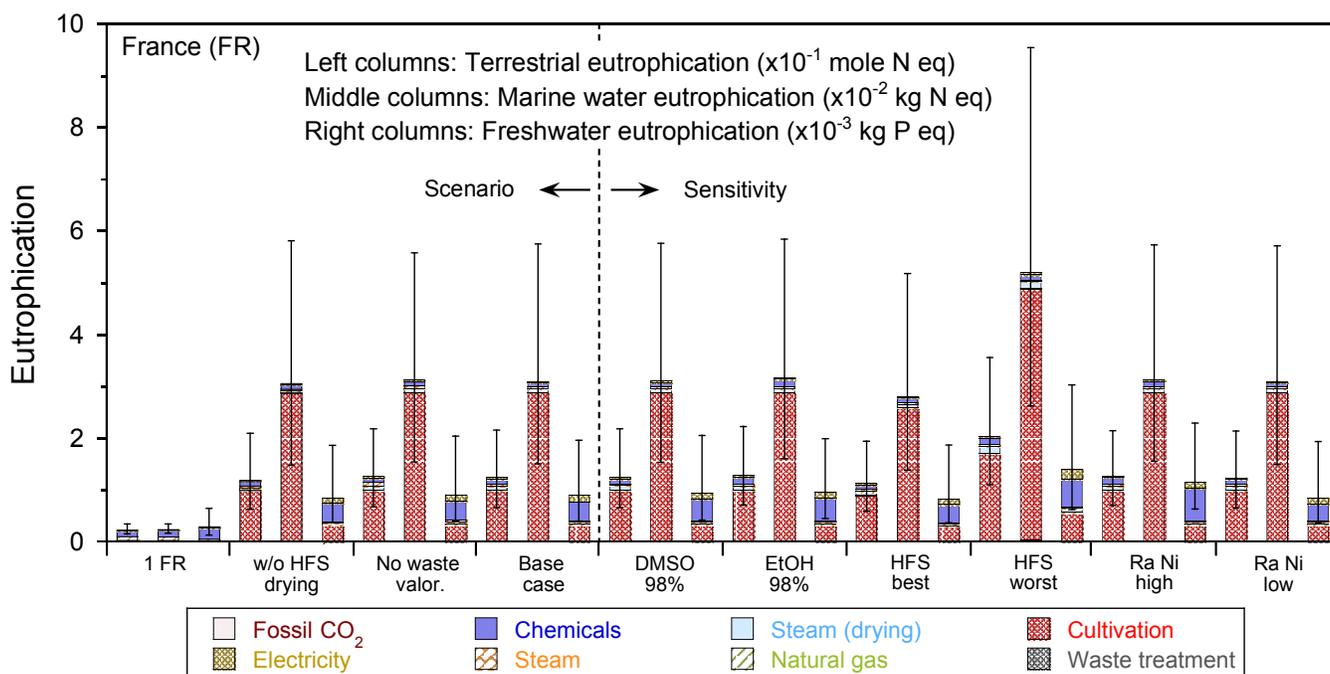


Fig. 9. Influence of HMDA production scenarios (left) and process variables (right) on terrestrial, marine and freshwater eutrophication (midpoint categories 6-8, respectively) for bio-based route 3P FR vs. 1 FR. The error bars (for a 95% confidence interval) were estimated with the SimaPro software using Monte Carlo simulations.

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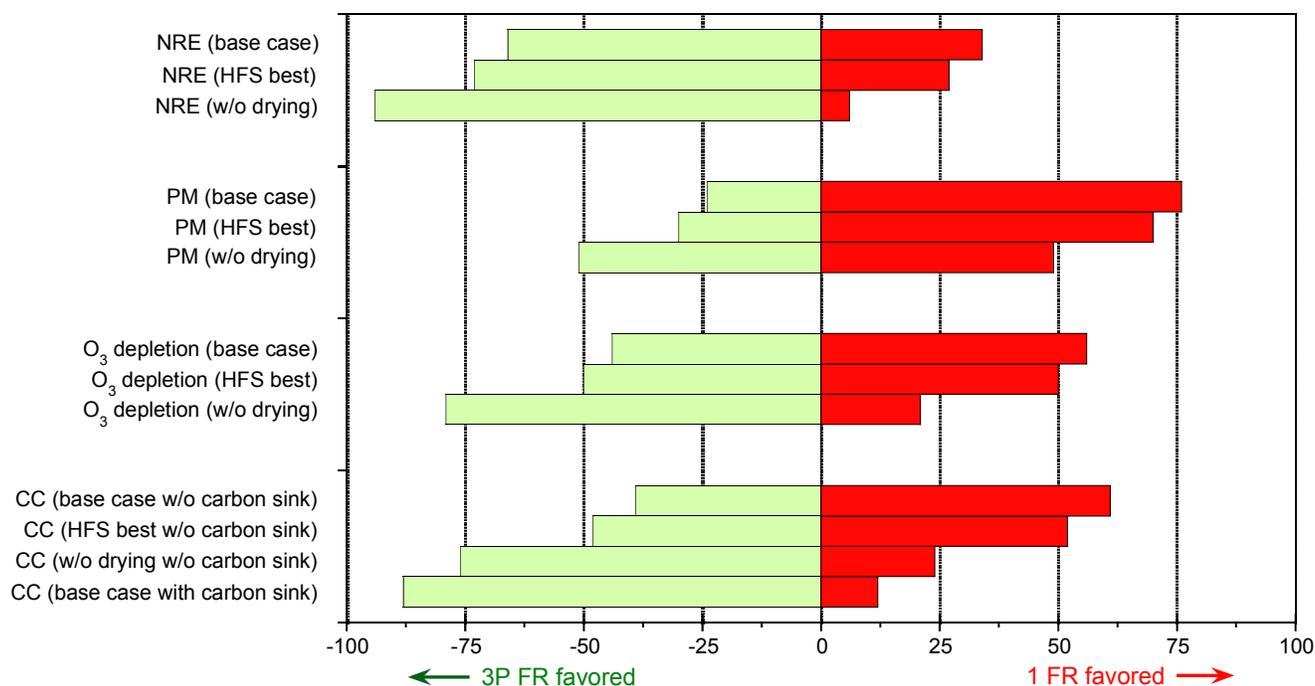


Fig. 10. Uncertainty analysis for bio-based route 3P FR vs. 1 FR unveiling the statistical significance of the values measured for non-renewable energy (NRE), particulate matter (PM), O₃ depletion, and climate change (CC) with and w/o carbon sink for base case, high HFS → HMF yield and w/o HFS drying.

Despite the high absolute uncertainty for each impact factor, some preliminary conclusions can be drawn on the differences between routes 3P FR and 1 FR for the three different scenarios (see Fig. 10 and examples of log-normal plots for the category climate change in Fig. S18). First, regarding Climate Change without taking into account the carbon sink, neither scenario shows an advantage of route 3P FR vs. 1F. However, when the carbon sink is taken into account one can notice a clear advantage of route 3P FR vs. 1 FR. As a matter of fact, 88%, 91% and 98% MC runs better for the base-case, HFS best and w/o HFS drying scenarios respectively.

Discussion

In the Results section, we have addressed the main shortcomings both in terms of cost and environmental footprint of the three projected bio-based paths compared to the well-established Dupont process for HMDA production. Noteworthy, we can anticipate even a larger gap with the benchmark if we consider the higher efficiency of new petro-based HMDA process generations. Furthermore, despite our comprehensive inventory for the bio-based paths, this is unavoidably incomplete due to the lack of detailed data and the strong assumption of full separation efficiency of the different intermediates.

Our LCA analysis reflects the potential benefits of the bio-based paths in terms of CO₂ footprint when the carbon sink is taken into account, but at the expense of a higher impact in terres-

trial, marine and freshwater eutrophication. Accordingly, the sustainability of bio-based paths should be regarded, at least in a first step of eco-design, as a tradeoff between these categories. More specifically, the major limitation of the above stated bio-based paths can be ascribed both to the feedstock used for fructose production, and the energy intensive drying of raw materials (e.g., with steam). On the one hand, maize and potato feedstocks entail a high environmental footprint, this being amplified during HMDA manufacture (i.e. 2.08 kg dry HFS for 1 kg HMDA for 3P FR route vs. 0.545 kg BD for 1 kg HMDA for 1FR route, see Table S1). Switching maize and potatoes to other feedstocks such as rice and wheat is not expected to reduce the environmental impact of the bio-based paths. On the other hand, HFS production from starch encompasses significant amounts of water (35 wt.% slurry), which must be removed, amplifying the environmental footprint of HMDA. Indeed, 2.6 kg starch is needed for 1 kg HMDA, involving 4.8 kg of water per kg HMDA (3P FR route), a major part of which must be removed by evaporation (e.g., use of steam).

From the analysis above, the use of fructose issued from maize and potato feedstocks for HMDA manufacture seems neither economically feasible nor sustainable. As an alternative, using the information issued from this study, we could foresee the eco-design of bio-based paths starting from fructose or glucose issued for instance from agricultural lignocellulosic waste. Such an approach might not only lead to more sustainable solutions, but also avoid the direct use of high-added value feedstocks, which

can be subjected to price volatility. However, such processes are not mature to date and their environmental benefit needs to be demonstrated. Furthermore, to secure and stabilize the manufacturing cost of chemicals from biomass, one could imagine a higher integration level of chemical companies in biorefineries.

Any potential process starting from biomass (including waste) for HMDA manufacture needs necessarily large amounts of water as in the case of the transformation of starch into fructose. Water needs to be removed later during the process to isolate HMDA. To this aim, one could imagine an alternative process where biomass instead of fossil fuels is used for steam generation. One could imagine as well a process where most of the water would be removed using mechanical separation (e.g., decantation, centrifugation, filtration). Minimizing the drying steps could certainly reduce the production cost and the environmental footprint of bio-HMDA. For instance, one could start from a diluted fructose syrup with a composition around 45 wt.% to produce the intermediate HMF in aqueous solution without using DMSO as solvent. Note that HMF synthesis in aqueous solution has been addressed in the literature.³⁶ In such a situation, the potential environmental benefits would correspond to the values indicated in Fig. 10 (i.e. rows w/o HFS drying).

Finally, we would like to stress that alternative bio-based routes for HMDA production without using neither HMF nor bio-butadiene as intermediate building blocks could be in principle foreseen (Fig. S1). However, to our knowledge, comparative life-cycle assessment studies on all these routes are not available to date.

Conclusions

Along this study, we have shown that the conventional fossil-based route for HMDA manufacture (hydrocyanation of butadiene) appears overall more economical and environmentally friendly than the three alternative bio-based paths considered in this study relying on HMF as building block. A sensitivity analysis shows that at least one of the three bio-based routes could be competitive in terms of cost compared to the fossil-based benchmark if either one of the following conditions is fulfilled: (1) BD price >1.8 €/kg, and (2) HFCS42% price <0.3 €/kg). As for the environmental impact, the best bio-based path (i.e. 3P FR) shows a clear advantage over the fossil-based route 1FR for the category Climate Change when the carbon sink is taken into account. However, a significant degradation of terrestrial, marine and freshwater eutrophication can be foreseen for the bio-based paths.

The eco-design of alternative bio-based paths relying on HMF requires necessarily well-suited feedstocks and processes for fructose production (for instance lignocellulose issued from agricultural waste) that are not available to date. Furthermore, to secure and stabilize the manufacturing cost of chemicals from biomass, one could imagine a higher integration level of chemical companies in biorefineries. In light of the results presented in this study, we could anticipate two main factors conditioning the success of novel bio-based routes for HMDA manufacture and extensively other chemicals: (1) the availability of inexpensive and environmentally friendly building blocks issued from biomass, and (2) the reduction of the energy demand and environmental burden for the removal of water issued from downstream biomass conversion. Furthermore, alternative bio-based routes for HMDA production using neither HMF nor bio-butadiene as building blocks could be in principle foreseen. However, the economic and environmental benefits of these routes are yet to be demonstrated.

Glossary

ADN	Adiponitrile
AM-THF	2,5-bis(aminomethyl)tetrahydrofuran
BC	Base case
BD	Butadiene
CC	Climate Change
DE	Germany
DFP	2,5-diformylfuran
DS	Dry substance
EQ	Ecosystem Quality
FR	France
GHG	Greenhouse gas
HMDA	Hexamethylenediamine
HDO	1,6-hexanediol
HFCS42%	High fructose corn syrup (42 wt.% fructose on dry basis)
HFS	High fructose syrup
HH	Human Health
HMF	2,5-hydroxymethylene furfural
LCIA	Life Cycle Inventory Analysis
LCA	Life Cycle Assessment
M	Maize
NRR	Non Renewable Resources
NTOTP	Ni-tri-o-tolyl phosphite
P	Potato
PET	Polyethylene terephthalate
PVC	Polyvinyl chloride
THFDM	2,5-bis(hydroxymethyl)tetrahydrofuran
WM	Water Management

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Notes and references

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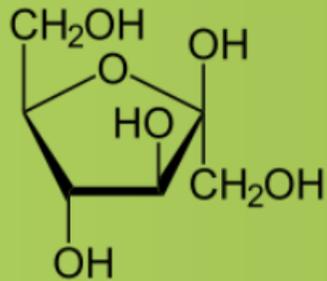
^b Solvay (China) Co., Ltd., 3966 Jin Du Rd., Xin Zhuang Industrial Zone, Shanghai 201108, PR China.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Starch



Fructose



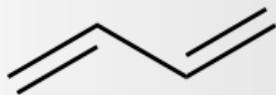
HMF



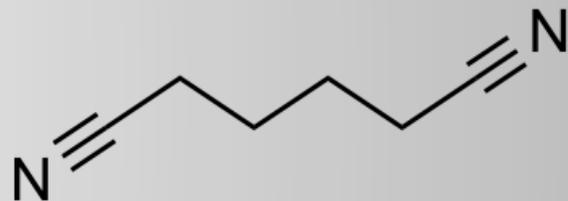
HMDA

Green Chemistry

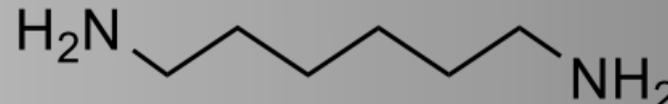
Economic & LCA Comparative Study



Butadiene



ADN



HMDA