

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

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ELECTRONIC SUPPORTING INFORMATION

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Fig. S15. Influence of HMDA production scenarios (left) and process variables (right) variables on photochemical ozone formation (midpoint category 4) for biobased 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. S16. Influence of HMDA production scenarios (left) and process variables (right) variables on acidification (midpoint category 5) for biobased 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. S17. Influence of HMDA production scenarios (left) and process variables (right) variables on non-renewable energy (midpoint category 9) for biobased 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. S18. Log-normal plots issued from Monte Carlo analysis for climate change (w/o carbon sink) comparing routes 3P FR and 1 FR. Scenarios: A) Base case, B) HFS best, and C) w/o drying.

Table S1. HMDA process inventory for the base case (see **Table 1** in main text) for the routes (1) to (4) and for the intermediates: HCN (1), 1,6 HDO (2), THFDM (3), DFF (4), AM-THF (3) and AM-THF (4). Consumptions (or generations) are indicated for the raw materials, by-products and wastes in kg/kg product, for the catalysts in g/kg product and for the utilities in their respective units per kg of product (i.e. HMDA or above-mentioned intermediates). Prices of raw materials and by-products are indicated with their bibliographic references.

Table S2. Process inventory of HFS production (dry basis, base case) from starch made from corn or potato.

Table S3. Molar yield for the reaction of HFS to HMF from values indicated in literature.

Table S4. Physicochemical properties of the main chemicals considered in this study for the three biobased routes.

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Table S6. Scores used for the Pedigree matrix to assess the quality of data sources (derived from ref.²⁸)

PROCESS DETAILS

Route 1: HMDA from butadiene and hydrogen cyanide (Fig. 1 in main text)

The most extended process for HMDA production proceeds *via* the hydrocyanation of butadiene. Since hydrogen cyanide (HCN) is highly toxic, its production is usually made captively on site. The PEP yearbook 2012 (“process economics program”, IHS Chemical) describes the manufacture of HCN according to the Andrussow process with methane and ammonia,¹ whereas a Dupont process is referred to for HMDA production from the hydrocyanation of butadiene.² The unit consumptions of items indicated in the process inventory (**Table S1**) for HCN and BD have been adapted from the PEP yearbook 2012.

In the Andrussow process, methane (natural gas), ammonia and air are reacted over a Pt/Rh catalyst at near flame conditions. The reactor is operated at 2 atm and at a temperature approaching 1090 °C. The catalyst consumption is very low, about 1 g/t HCN. The total conversion per pass is about 75% for ammonia and 97% for methane. H₂, N₂ and CO are the by-products. A burner is used to convert CO into CO₂ before release into atmosphere. Unconverted ammonia is recovered by quenching the reactor effluent with aqueous ammonium dihydrogen phosphate. The diammonium hydrogen phosphate formed is distilled to recover the ammonia for recycling. HCN is recovered from the gases leaving the quench tower by absorption in chilled water. The aqueous HCN is then fractionated to give a liquid product with a purity >99%. The overall yield is about 60% based on methane and 84% based on ammonia.¹

The PEP yearbook 2012 gives the following process summary for the HMDA production from butadiene according to the Dupont process. It is worthwhile to note that this model is quite approximate and not fully representative of the new generations of HMDA processes. Butadiene and hydrogen cyanide react at 80 °C and 7.8 atm using a Ni-tri-*o*-tolylphosphite (NTOTP) catalyst to form pentenenitriles (PNs) and unconverted reactants are recycled. PNs are distilled to remove methyl-butenenitrile, which is isomerized into PNs over a Ni catalyst and distilled for PNs recovery. PNs from hydrocyanation and isomerization are hydrocyanated to adiponitrile (ADN) at 41-65 °C and 1 atm using a NTOTP catalyst and triphenylborane (TPB) promoter. After PN separation, the reaction product is extracted with cyclohexane to separate NTOTP, which is recovered by evaporating the cyclohexane. The raffinate is distilled to recover PNs for recycling, to remove ADN isomers, and to recover ADN. The spent catalyst and TBP are recovered by a series of steps, including ammoniation, evaporation, calcination, and reaction with tri-*o*-tolylphosphite. Further hydrogenation of the ADN into HMDA can be carried out in the temperature range 90-200° C under hydrogen pressure of about (range 250-400 atm) in the presence of ammonia in an ammonia-to-ADN weight ratio of at least about 1.8/1. The product yield is about 85% based on butadiene and 88.7% based on HCN.²

Starch to HFS (Fig. 2 in main text)

The environmental footprint of the manufacture of HFS from starch could not be found in public databases. As a result, a model was built in order to assess the environmental impacts, which is based on patents,³ and on a IHS Chemical report.⁴ HFS can be manufactured from starch on a continuous enzymatic process at atmospheric pressure using the following enzymes and operational conditions

- Alpha-amylase to break and shorten the long carbon chains of the raw starch. The enzyme is fed continuously to the reactor (1.5 h, 120 °C max, atmospheric pressure).
- Glucoamylase to break the chains down into glucose. The enzyme is fed continuously to the reactor (60 °C for 48 h).
- Xylose isomerase (glucose isomerase) to convert the glucose into a mixture of about 42% fructose, 52% glucose and 6% other sugars (fixed bed reactor, 4 h, 60 °C). The composition remains the same whatever the starch source (*i.e.* corn or potato).

HFS to HMF (Fig. 2 in main text)

Recent publications suggest the possibility of converting fructose into HMF in water solution to get a final aqueous HMF solution.⁵ However, the present state-of-the-art points to the use of DMSO solvent for

HMF production to reach higher yields.⁶ Water could actually be a reactant: it plays a role in the reversion equilibrium and in HMF hydrolysis.⁶

In our calculations, we assumed a yield for the transformation of HFCS42% (dry) to HMF lying in the range 49-88% (Table S3), which are typical laboratory yields that could be representative of industrial values. A yield >87% is commonly achieved at laboratory scale for the transformation of fructose into HMF. However, the reaction of the glucose contained in HFS has been reported as far more difficult.⁷ To our knowledge, the best reported yield is 81%.⁸ In our case, we took a mean yield of 83.5% for 100% conversion of HFS (selectivity of 87% for fructose and selectivity of 81% for glucose and other sugars in HFCS42% in HFS).

The HMF reaction would be made in a batch catalytic reactor at 120°C, atmospheric pressure, and for around 2 h in the presence of DMSO solvent with a mass ratio DMSO : HFS(dry) of 2.7 : 1.⁹ The water produced during dehydration would be continuously evaporated from the reactor to shift the reaction equilibrium towards HMF. A potential catalyst for the reaction could be a strong Lewis acid such as Cu(NTF₂)₂.¹⁰ We assume here as base case that 99% of catalyst could be recycled. The catalyst consumption would be then 1.54 g Cu(NTF₂)₂/kg HMF.

After the reaction, the following step is DMSO removal. A proper estimation can hardly be done due to the little information available on efficient workup procedures for the DMSO-HMF mixture. Earlier studies reported a high difficulty in using vacuum distillation to separate HMF from DMSO. The following techniques could be attempted: vacuum distillation, fractional melting and washing, re-crystallization from miscellaneous solvents such as water, diethyl ether and petroleum ether.⁶ Here we have chosen two consecutive vacuum distillation separations achieving pure HMF after the second unit: 1) DMSO distillation, (~130°C, 1 mbar), and 2) distillation of crude HMF containing humin impurities. An energy balance was applied to estimate roughly the steam consumption for these distillation units. A strong assumption was taken for the isolation of HMF: 100% HMF isolation yield and 99.9% recovery.

Route 2: HMF → THFDM → 1,6 HDO → HMDA (Fig. 2 in main text)

After examining various possibilities to obtain 1,6 HDO from HMF, Buntara et al. have come up with the route HMF → (THFDM) → 1,6 HDO as the most eco-friendly and economically feasible.¹¹ In this process, THFDM is obtained by hydrogenation of HMF in a batch catalytic reactor at 100 °C under 90 atm pressure for 14 h using ethanol as solvent (ethanol : HMF molar ratio of 7 : 1), hydrogen (H₂ : HMF molar ratio of 100 : 1) over a heterogeneous Ni catalyst. Hydrogen would be separated by decompression of the reactor and the ethanol by distillation. Then, another batch hydrogenation is implemented to get 1,6 HDO from THFDM at 120°C, 80 atm for 20 h in the presence of water as solvent (water : THFDM molar ratio of 10 : 1), hydrogen (H₂ : THFDM molar ratio of 100 : 1) over a heterogeneous Rh-Re/SiO₂ catalyst.¹² In absence of additional data, we assumed that the second hydrogenation step could be implemented in a fixed bed reactor with limited catalyst consumption: up to 0.1 g Rh-Re/SiO₂ per kg of HDO. Hydrogen might be removed from the product mixture by decompression and the water solvent might be separated by distillation. Another distillation step could be needed to split up the by-product 1,5-HDO from 1,6-HDO.

A US patent describes the next step of transformation of HDO into HMDA by high-pressure amination.¹³ HMDA would be obtained by a single-step continuous reaction (200°C, 25 atm, Raney Nickel) under an ammonia excess (NH₃ : HDO molar ratio of 5 : 1) and in the presence of hydrogen (H₂ : HDO molar ratio of 8 : 1). The HDO conversion would be 100% with a selectivity of 90%.¹⁴ The excess ammonia and hydrogen would be removed from the product liquid mixture by depressurization and then recycled. We foresee ca. 10 mol.% impurities, some remaining ammonia and reaction water in the final HMDA, which could be removed in several steps. First a distillation step would be used to recover ammonia. Cyclohexane would be further added to the crude HMDA and this would be dried in a column by evaporation of water and cyclohexane under a heteroazeotrope form (BP: 69.8°C). The heteroazeotrope would be then decanted to separate cyclohexane from water. Cyclohexane would be further recycled with an assumed 100% yield. A final distillation would be realized to remove the final impurities. HMDA would be finally crystallized (MP: 39°C) by cooling down to ambient temperature and drying. We foresee a HMDA purity of at least 99.5%.

Route 3: HMF → THFDM → AM-THF → HMD (Fig. 2 in main text)

The hydrogenation of HMF into THFDM has been described for route 2. The second step THFDM → AM-THF is comparable to 1,6 HDO amination into HMDA previously described. The third step consists of an opening of the AM-THF molecular ring by reaction over a hydrodeoxygenation catalyst in the presence of a halogenated solvent. Such a reaction has been recently addressed by Rennovia patent.¹⁵ The patent claims the possibility of converting tetrahydrofuran 2,5-dicarboxylic acid (THFDCA) into linear adipic acid molecule with a yield of 99% over a Pd catalyst supported on silica beads. The reaction was realized at 160 °C for 3 h under hydrogen iodide: THFDCA equimolar ratio. The reactor was pressurized with hydrogen until 48 atm. Here we have assumed that such reactions conditions and yield could be attained for the conversion of AM-THF into HMDA due to the very similar reaction mechanism. Finally, even if the Rennovia's patent¹⁵ does not tackle the separation step, we can reasonably propose that hydrogen iodide and H₂ gas could be recovered after reaction by reactor depressurization, re-compression and recycling into reactor. A recovery rate of 99.9% was assumed for hydrogen iodide as base case. After the reaction, the crude HMDA would be purified in a distillation column, crystallized and dried.

Route 4: HMF → DFF → AM-THF → HMD (Fig. 2 in main text)

The first step involves the oxidation of HMF into DFF. The second step involves the amination of DFF into AM-THF, which is similar to 1,6 HDO amination into HMDA previously described. The last step from AM-THF to HMDA has also been described previously.

Dealing with the first step, DFF may be produced industrially from the oxidation of pure HMF in an oxygenated solvent.^{14,16} Another option could start from a HMF mixture issued from the dehydration of HFS.¹⁷ The main advantage is that HMF is not extracted from the reaction mixture and the solvent used for the dehydration is also used for the oxygenation step. However, this one-pot reaction is more complicated. In our case, our choice was to model the first case starting from pure HMF. The oxidation (50 °C; atmospheric pressure; 8 h, MnO₂ catalyst) was assumed to be realized in a batch reactor (dichloromethane : HMF weight ratio of 8 : 1), achieving a yield to DFF of 80%. The catalyst might be then filtered, regenerated and recycled. The solvent might be further recovered by distillation and recycled with a 99.9% yield. The separation of unreacted HMF would be performed by a precipitation step. After the reaction, the dissolved mixture would be cooled to precipitate DFF. The HMF is expected to remain soluble in the liquid phase. The recovered HMF might be dried for water removal and recycled.

CHEMICAL REACTIONS FOR BIO-BASED ROUTES (2-4) (Fig. 2 in main text)

HFS → HMF (routes 2-4)

Dehydration HFS				
	$C_6H_{12}O_6$	+	$C_6H_{12}O_6$	$\xrightarrow{\text{Dehydration}} C_6H_6O_3 + 3H_2O$
Mw	180.2		180.2	126.1 18.0
Eq	1.1		1.1	1.1 3.3
	Fructose		Glucose	5-HMF Water

ROUTE 2: 5-HMF → THFDM → 1,6-HDO / 1,5-HDO → HMDA

5-HMF → THFDM				
	$C_6H_6O_3$	+	$3H_2$	$\xrightarrow{\text{Hydrogenation}} C_6H_{12}O_3$
Mw	126.1		2.0	132.2
Eq	1.1		3.3	1.1
	5-HMF		Dihydrogen	THFDM
THFDM → 1,6-HDO				
	$C_6H_{12}O_3$	+	$2H_2$	$\xrightarrow{\text{Hydrogenation}} C_6H_{14}O_2 + H_2O$
Mw	132.2		2.0	118.2 18.0
Eq	1.1		2.2	1.1 1.1
	THFDM		Dihydrogen	1,6-HDO Water
THFDM → 1,5-HDO (side reaction)				
	$C_6H_{12}O_3$	+	$2H_2$	$\xrightarrow{\text{Hydrogenation}} C_6H_{14}O_2 + H_2O$
Mw	132.2		2.0	118.2 18.0
Eq	0.2		0.4	0.2 0.2
	THFDM		Dihydrogen	1,6-HDO Water
1,6-HDO → HMDA				
	$C_6H_{14}O_2$	+	$2NH_3$	$\xrightarrow{\text{Amination}} C_6H_{16}N_2 + 2H_2O$
Mw	118.2		17.0	116.2 18.0
Eq	1.1		2.2	1.1 2.2
	1,6-HDO		Ammonia	HMDA Water

ROUTE 3: 5-HMF → THFDM → AM-THF → HMDA

5-HMF → THFDM				
	$C_6H_6O_3$	+	$3H_2$	$\xrightarrow{\text{Hydrogenation}} C_6H_{12}O_3$
Mw	126.1		2.0	132.2
Eq	1.1		3.3	1.1
	5-HMF		Dihydrogen	THFDM
THFDM → AM-THF				
	$C_6H_{12}O_3$	+	$2NH_3$	$\xrightarrow{\text{Amination}} C_6H_{14}N_2O + 2H_2O$
Mw	132.2		17.0	130.2 18.0
Eq	1.1		2.2	1.1 2.2
	THFDM		Ammonia	AM-THF Water
AM-THF → HMDA				
	$C_6H_{14}N_2O$	+	$2H_2$	$\xrightarrow{\text{Hydrodeoxygenation}} C_6H_{16}N_2 + H_2O$
Mw	130.2		2.0	116.2 18.0
Eq	1.1		2.2	1.1 1.1
	AM-THF		Dihydrogen	HMDA Water

ROUTE 4: 5-HMF → DFF → AM-THF → HMDA

5-HMF → DFF					
	$C_6H_6O_3$	+	$0.5O_2$	$\xrightarrow{\text{Oxidation}}$	$C_6H_4O_3 + H_2O$
Mw	126.1		32.0		124.1 18.0
Eq	1.1		0.6		1.1 1.1
	5-HMF		Dioxygen		DFF Water
DFF → AM-THF					
	$C_6H_4O_3$	+	$2NH_3$	+	$4H_2 \xrightarrow{\text{Red.amination}} C_6H_{14}N_2O + 2H_2O$
Mw	124.1		17.0		2.0 122.1 18.0
Eq	1.1		2.2		4.4 1.1 2.2
	DFF		Ammonia	Dihydrogen	AM-THF Water
AM-THF → HMDA					
	$C_6H_{14}N_2O$	+	$2H_2$	\xrightarrow{HDO}	$C_6H_{16}N_2 + H_2O$
Mw	130.2		2.0		116.2 18.0
Eq	1.1		2.2		1.1 1.1
	AM-THF		Dihydrogen		HMDA Water

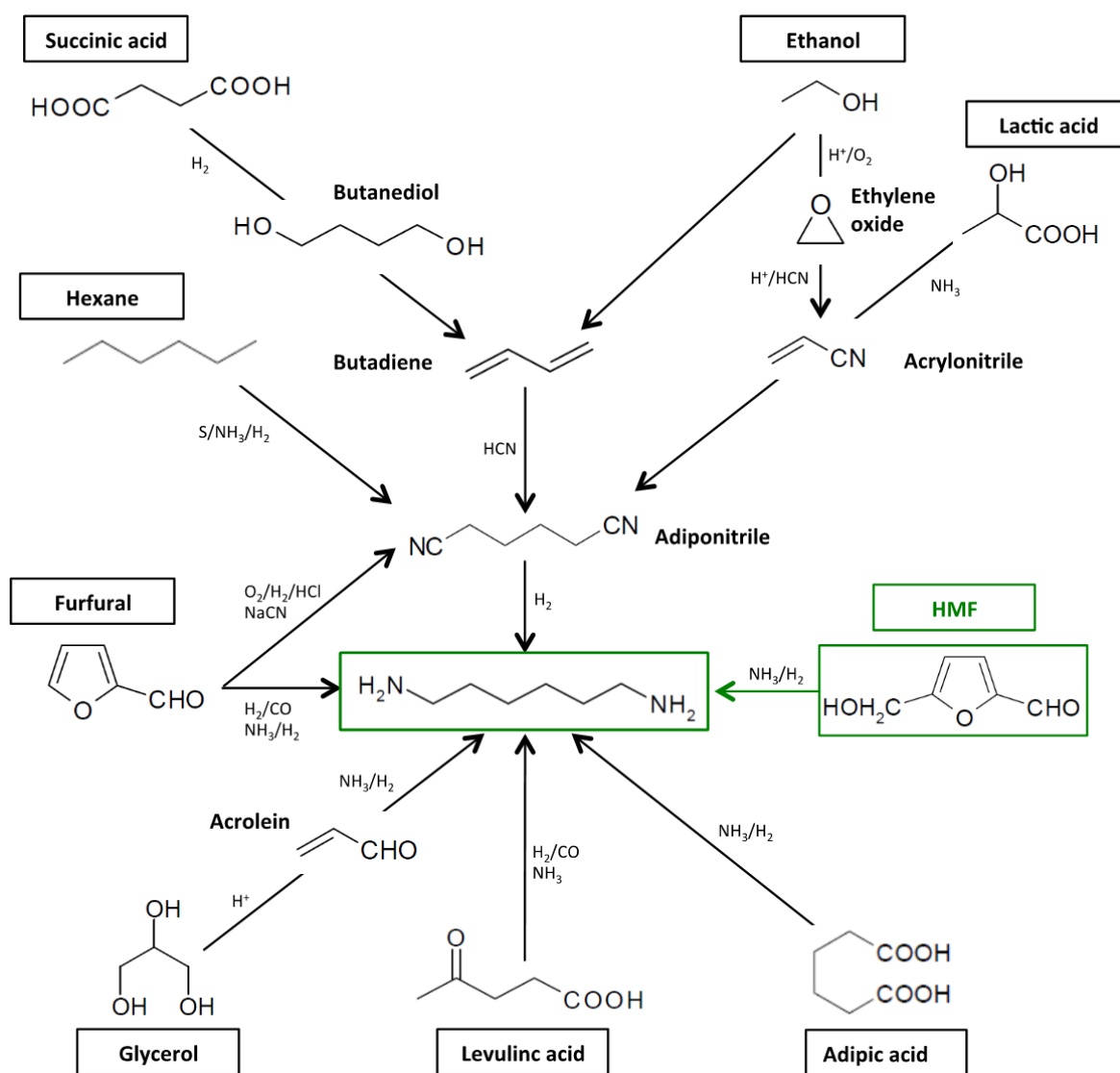


Fig. S1. Speculative routes for the production of bio-based HMDA using molecules issued from biomass.

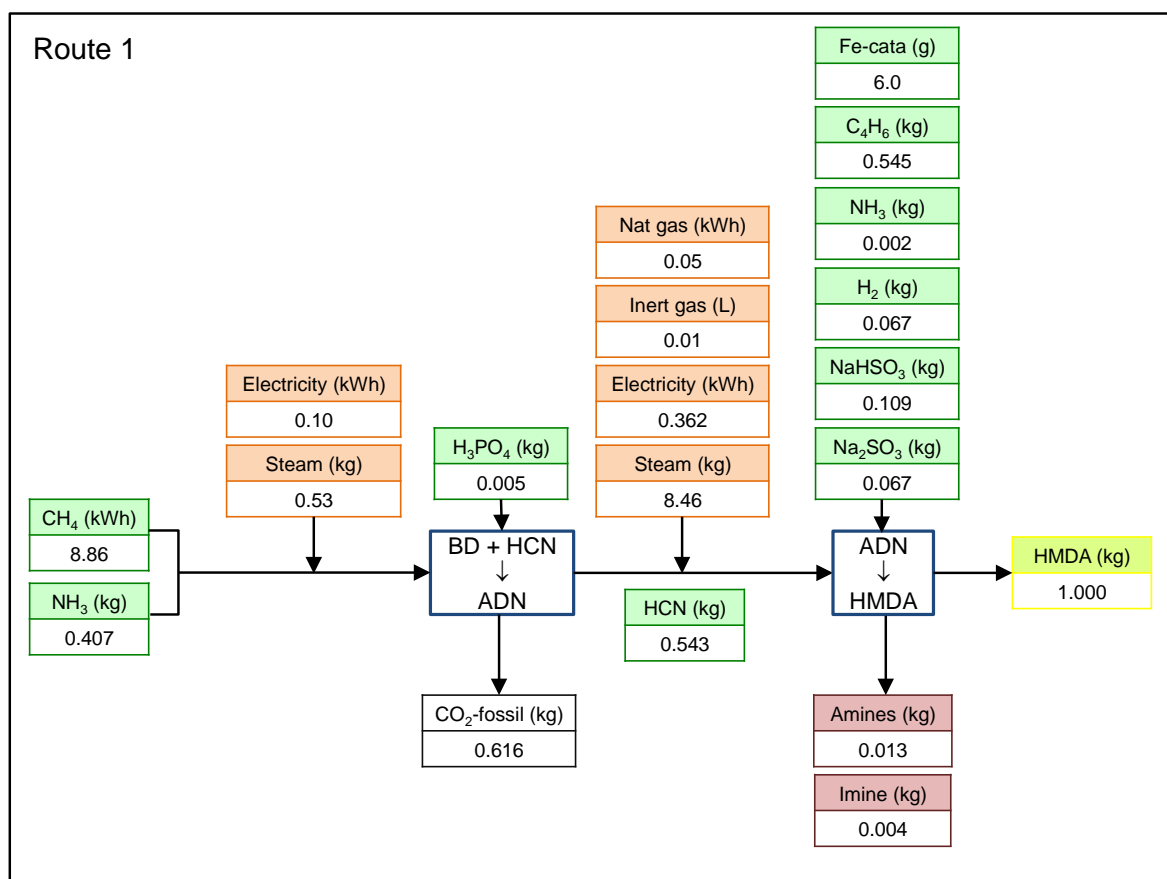


Fig. S2. Flowsheet for the fossil-based route 1.

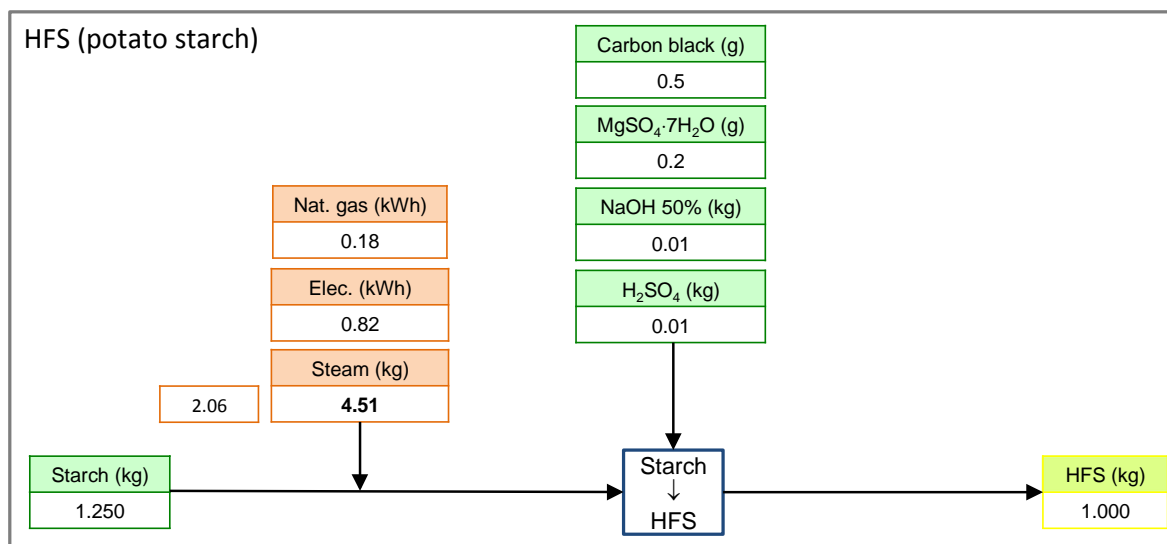


Fig. S3. Flowsheet for the initial route Starch → HFS. The bold number corresponds to the base-case value for steam consumption used in the LCA sensitivity study. The w/o HFS drying scenario value is also indicated.

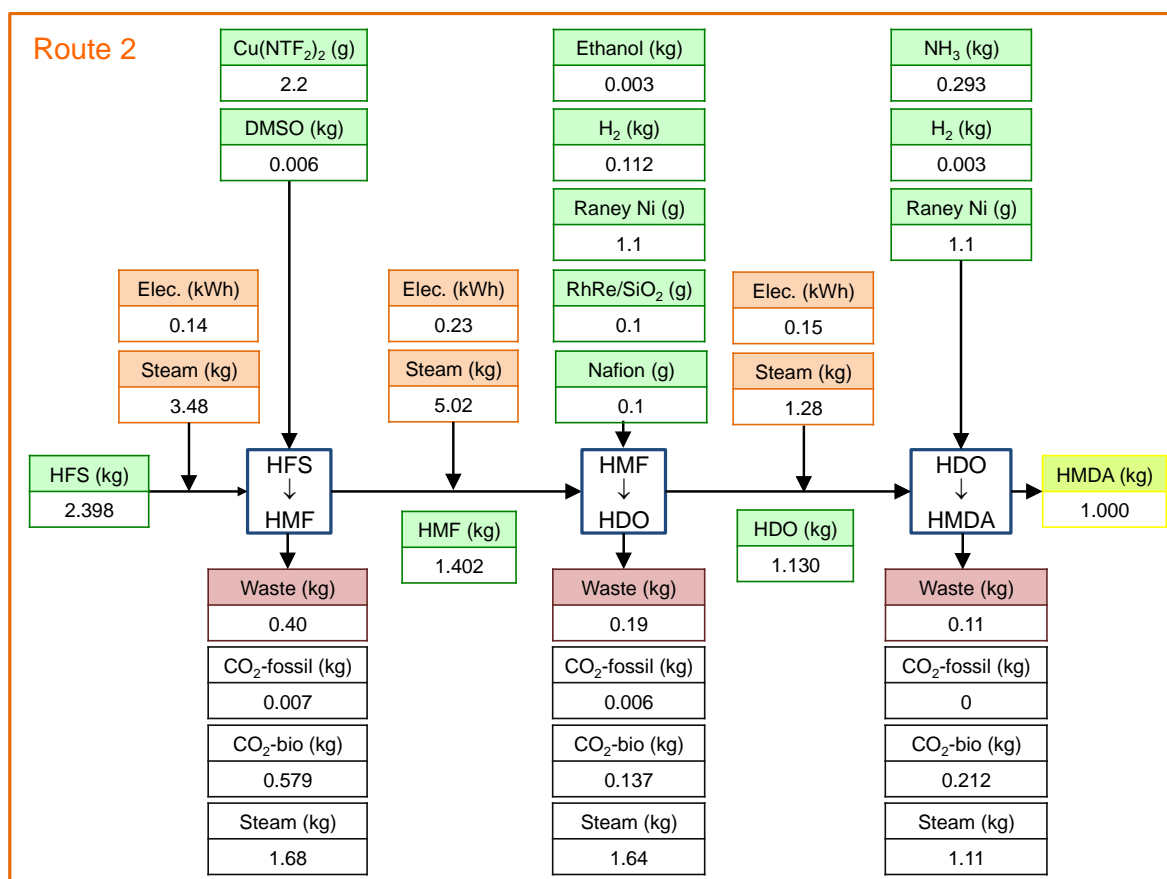


Fig. S4. Flowsheet for the bio-based route 2.

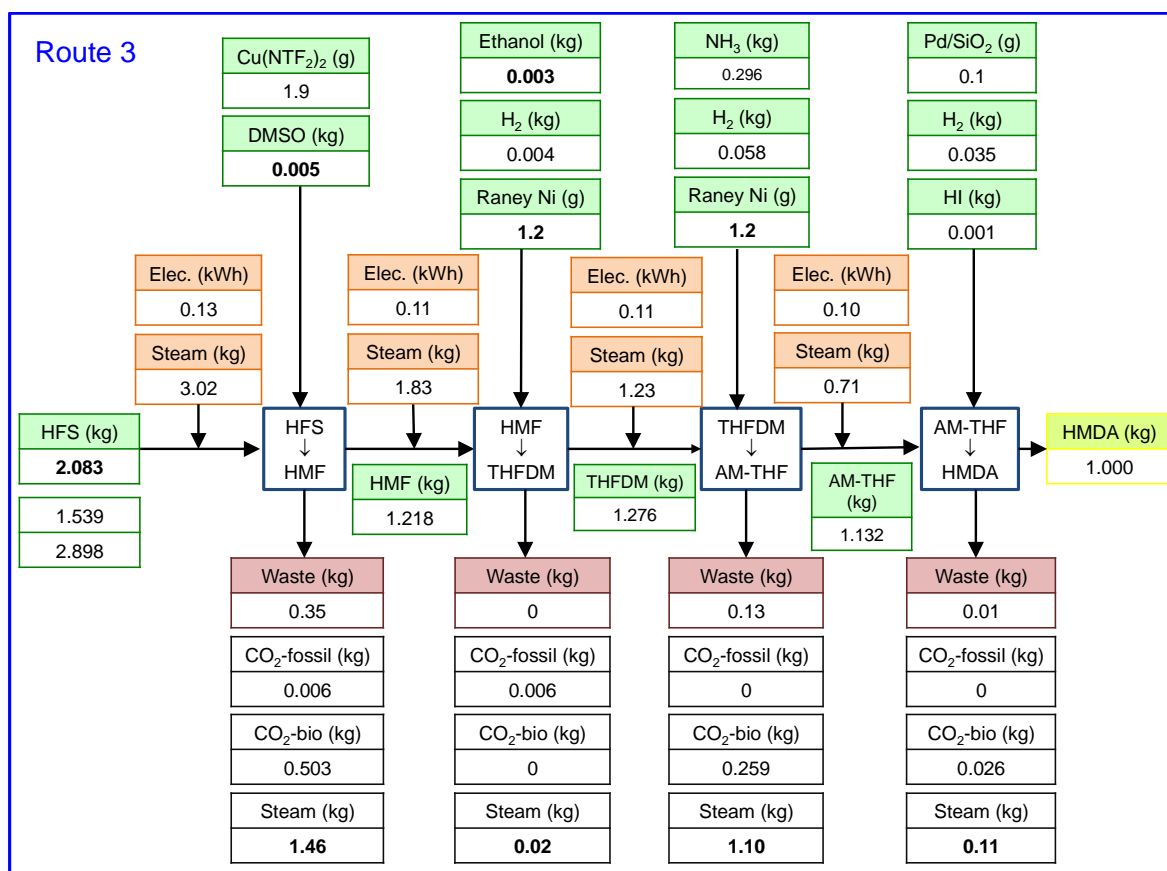


Fig. S5. Flowsheet for the bio-based route 3. The bold numbers correspond to the base-case values used in the LCA sensitivity study. For HFS, the best- and worst case scenario values are also indicated.

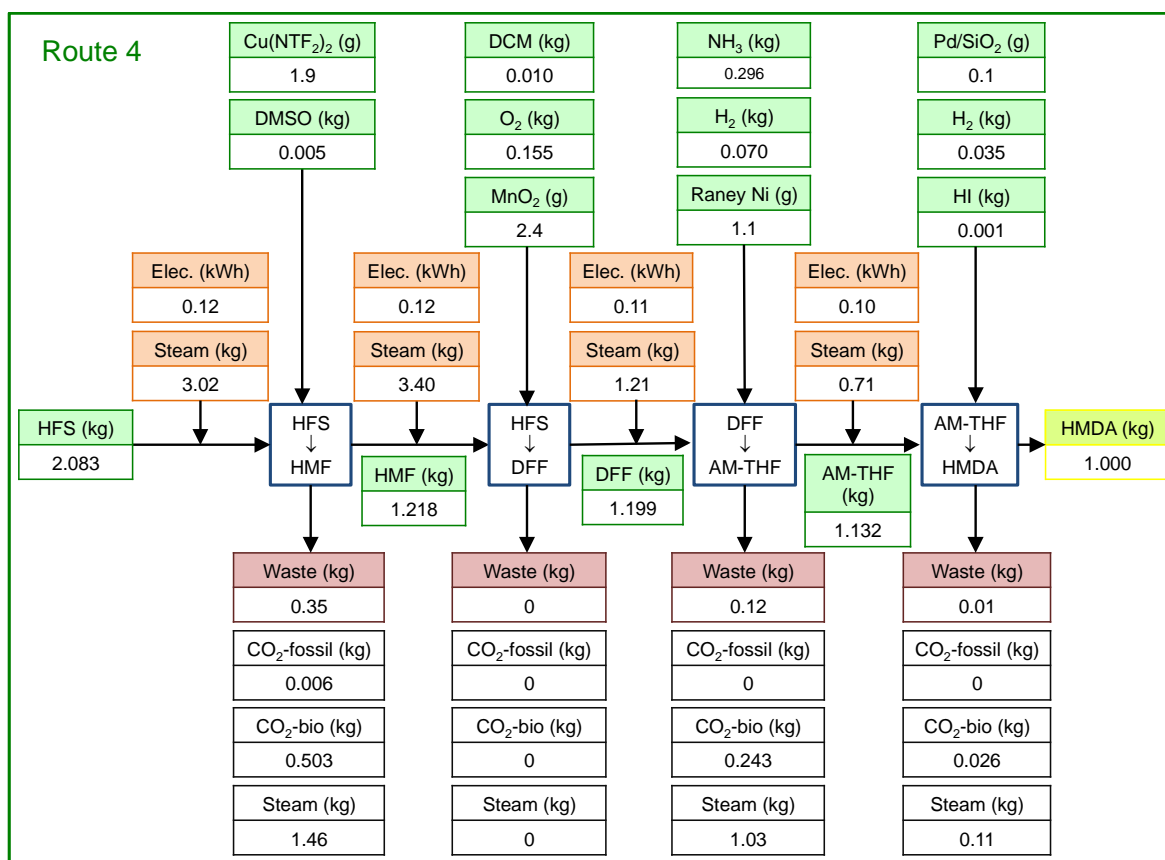


Fig. S6. Flowsheet for the bio-based route 4.

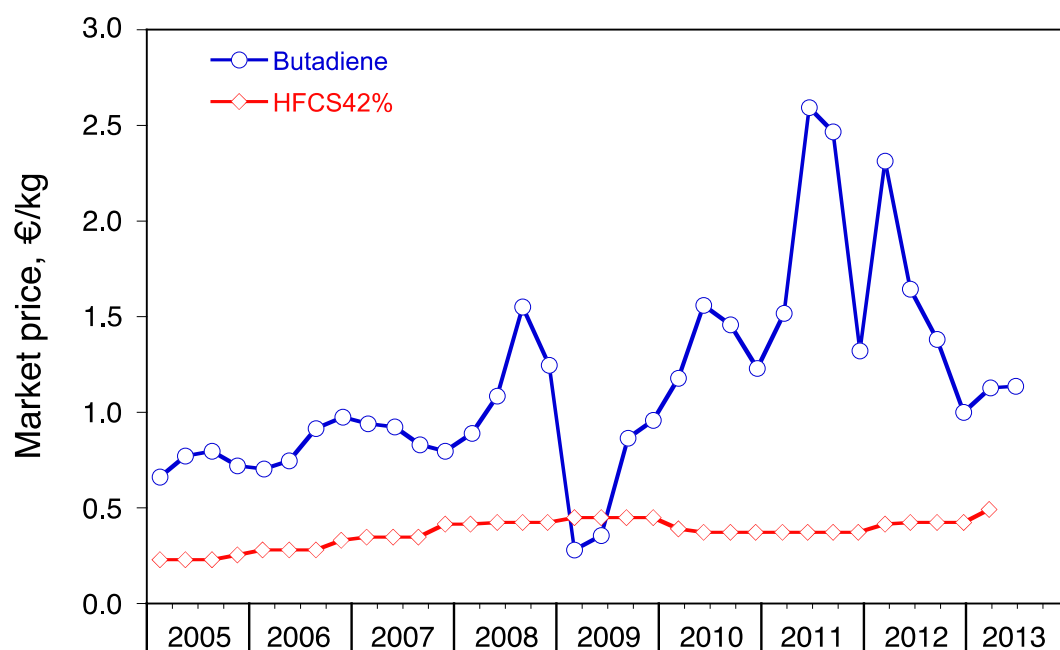


Fig. S7. Evolution of the market price of butadiene and HFCS42%. Data obtained from ref.¹⁸ and ref.²¹, respectively.

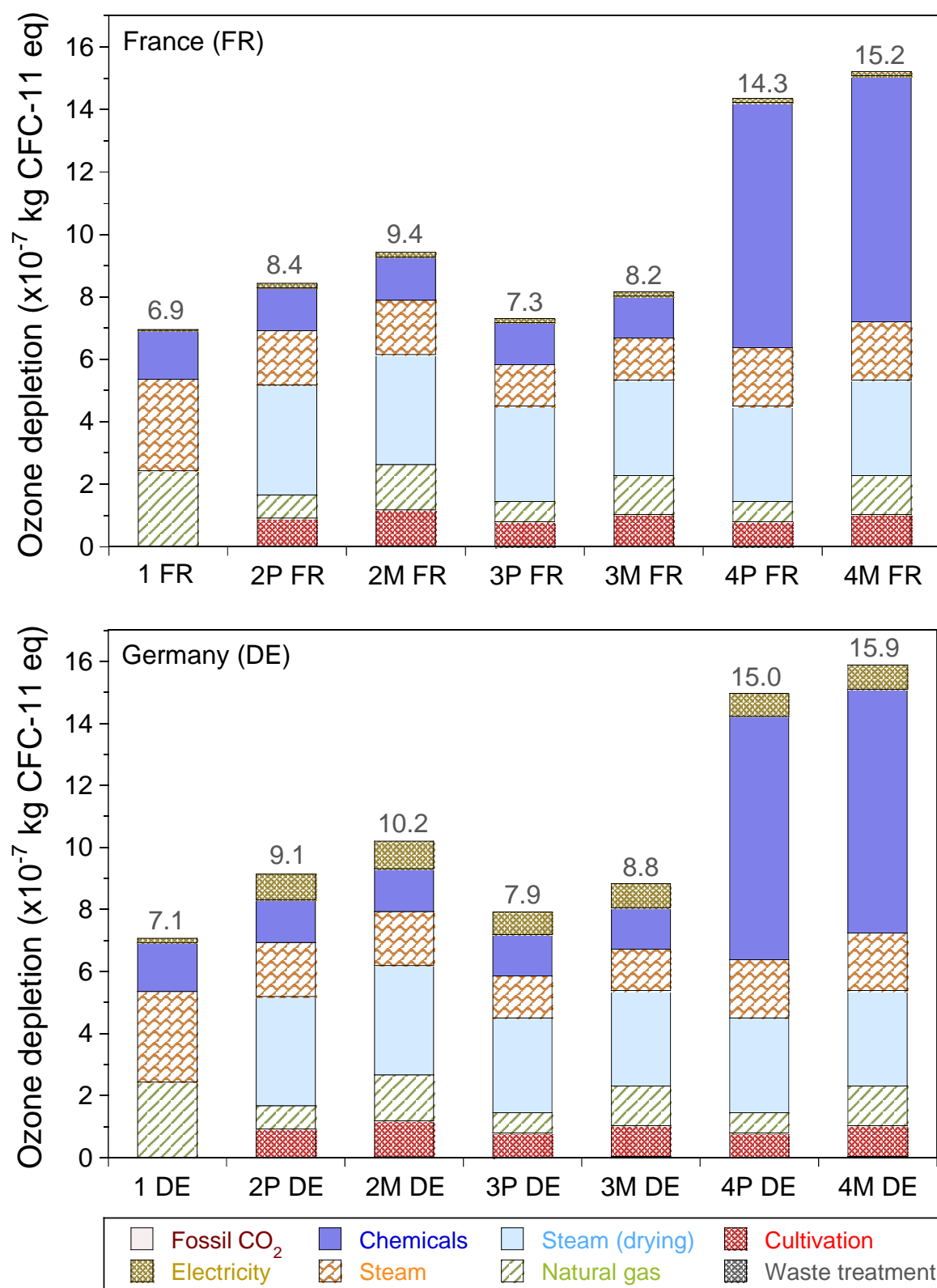


Fig. S8. Impact score breakdown for ozone depletion (midpoint category 2) for HMDA production in France and Germany.

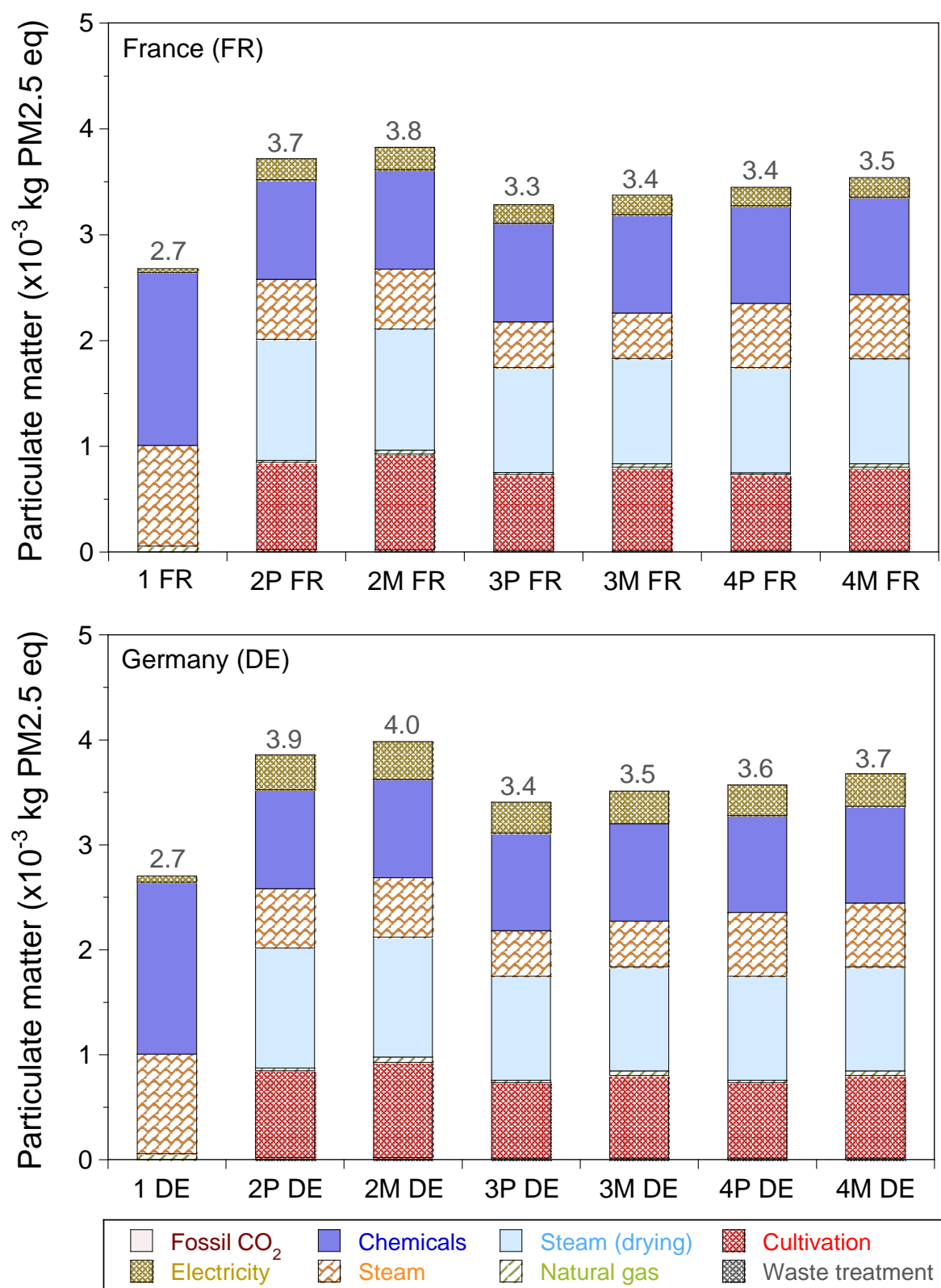


Fig. S9. Impact score breakdown for particulate matter (midpoint category 3) for HMDA production in France and Germany.

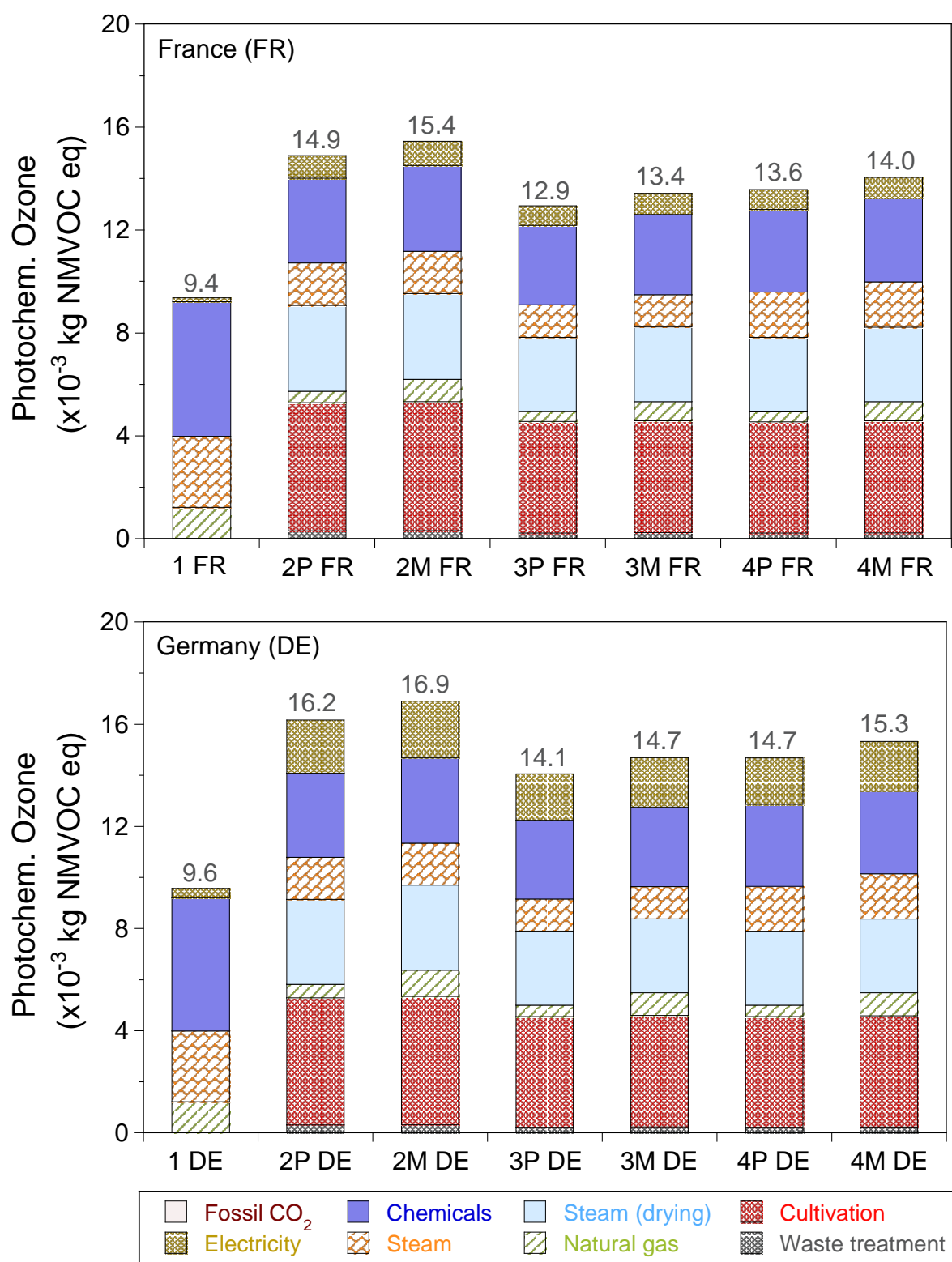


Fig. S10. Impact score breakdown for photochemical ozone formation (midpoint category 4) for HMDA production in France and Germany.

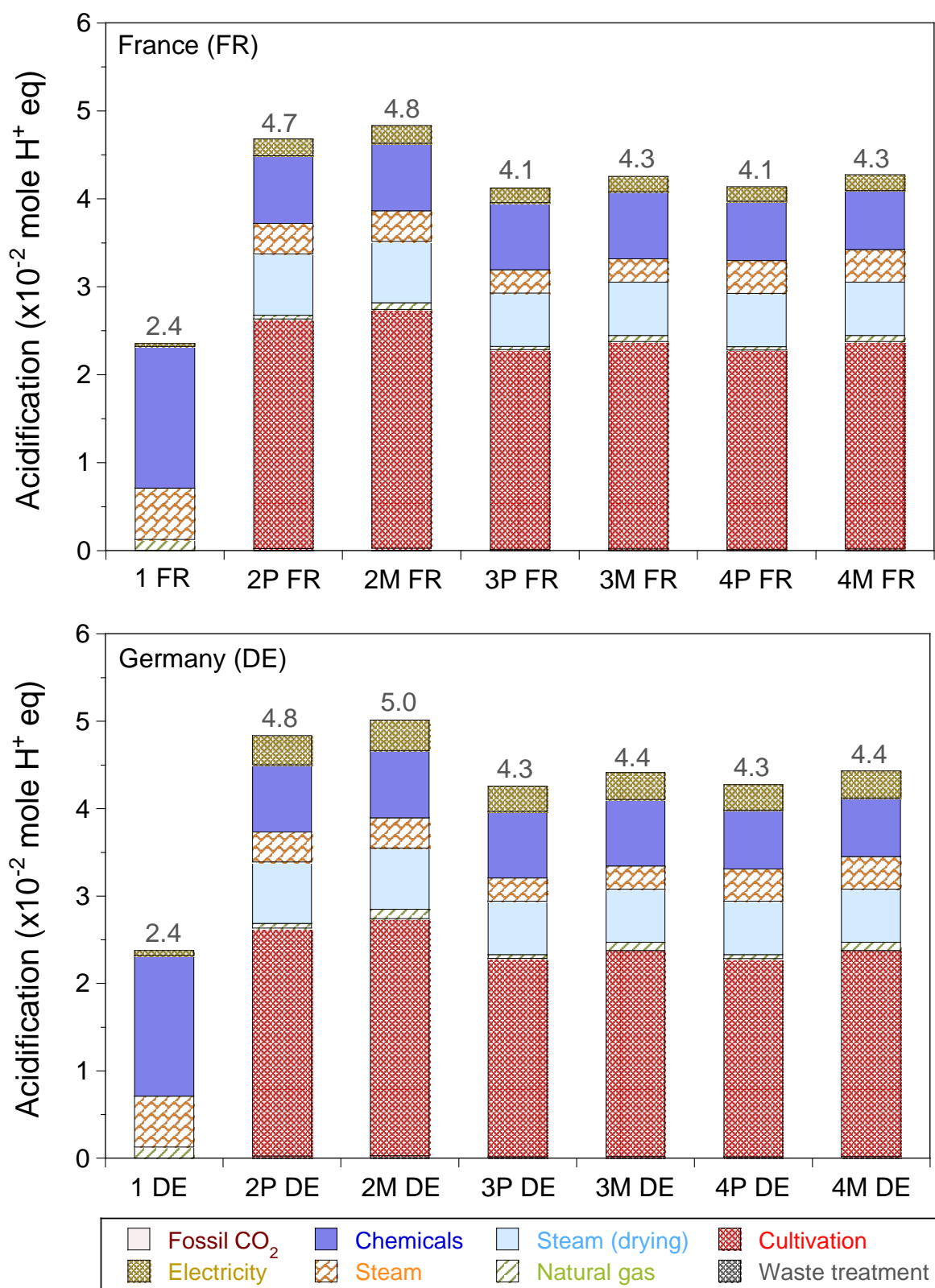


Fig. S11. Impact score breakdown for acidification (midpoint category 5) for HMDA production in France and Germany.

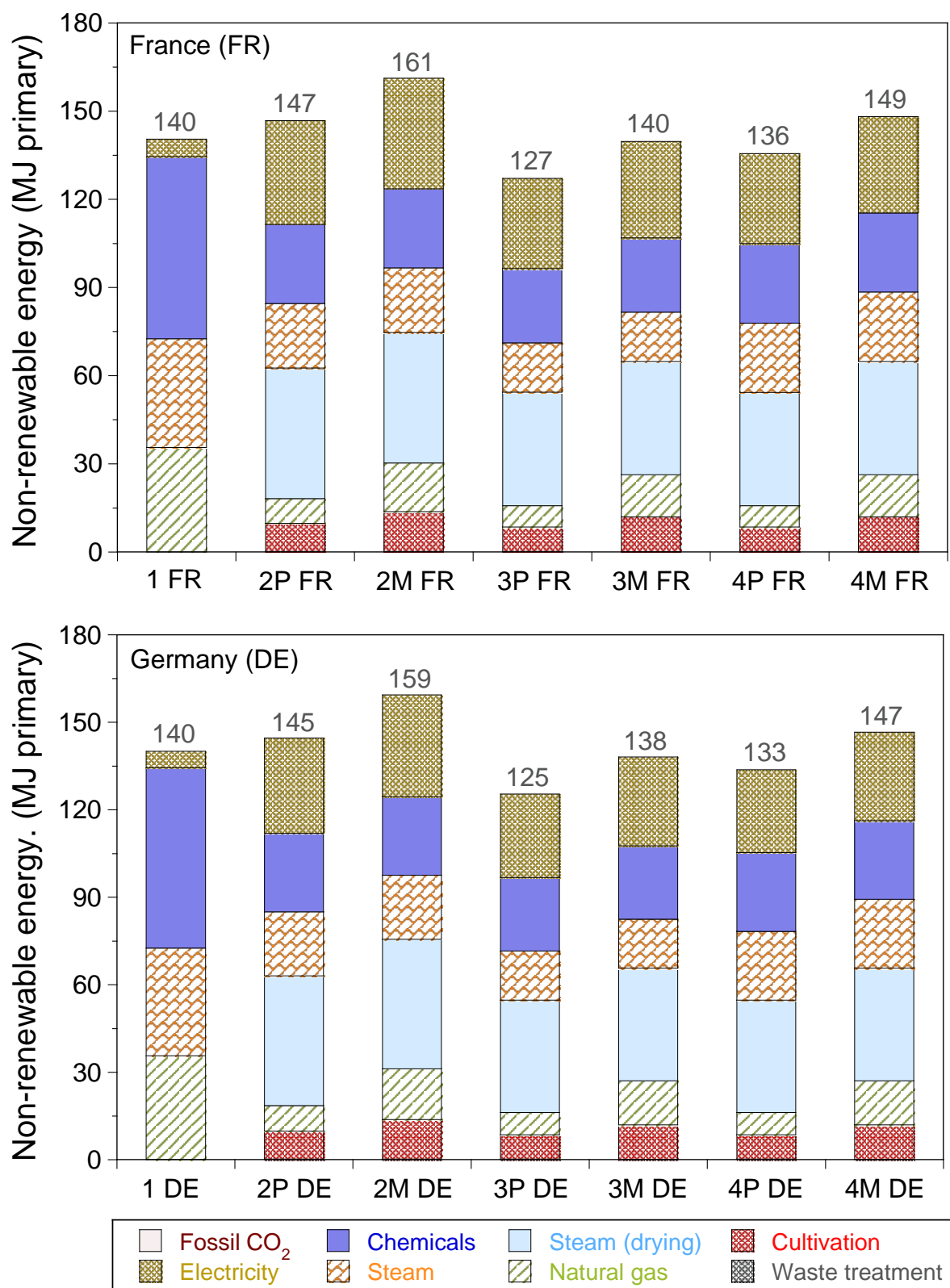


Fig. S12. Impact score breakdown for non-renewable energy (midpoint category 9) for HMDA production in France and Germany.

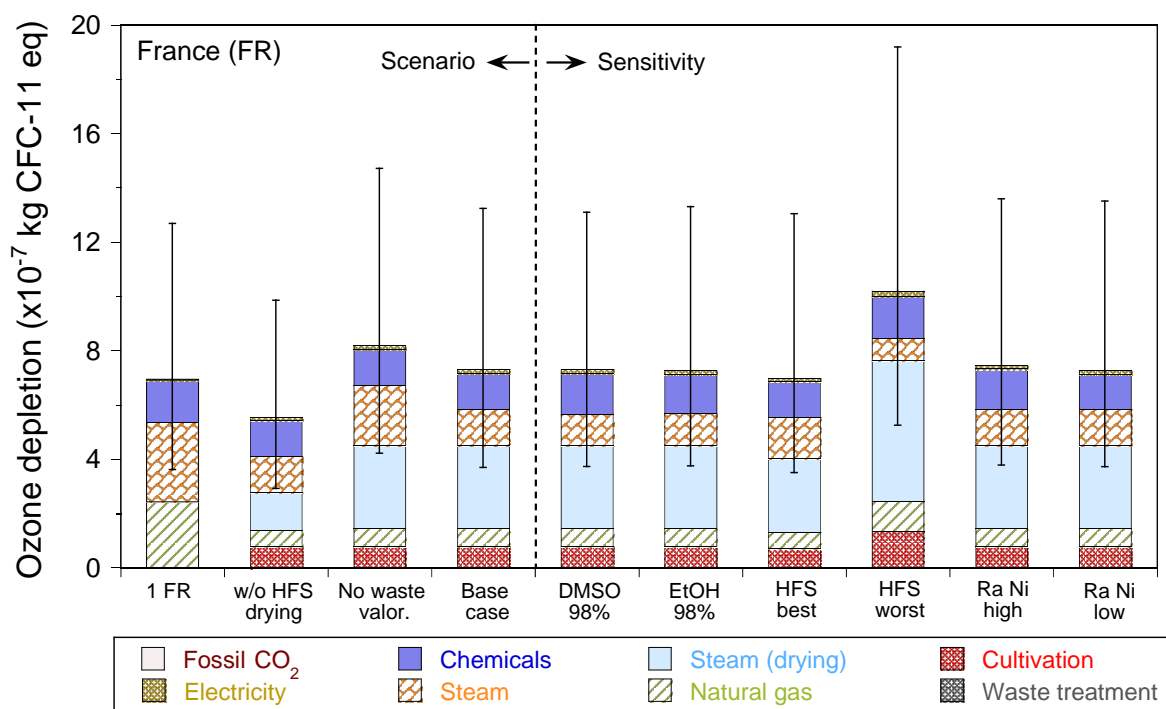


Fig. S13. Influence of HMDA production scenarios (left) and process variables (right) on ozone depletion (midpoint category 2) for biobased route 3P FR vs. 1 FR. The error bars were estimated using the Monte Carlo tool available in SimaPro software.

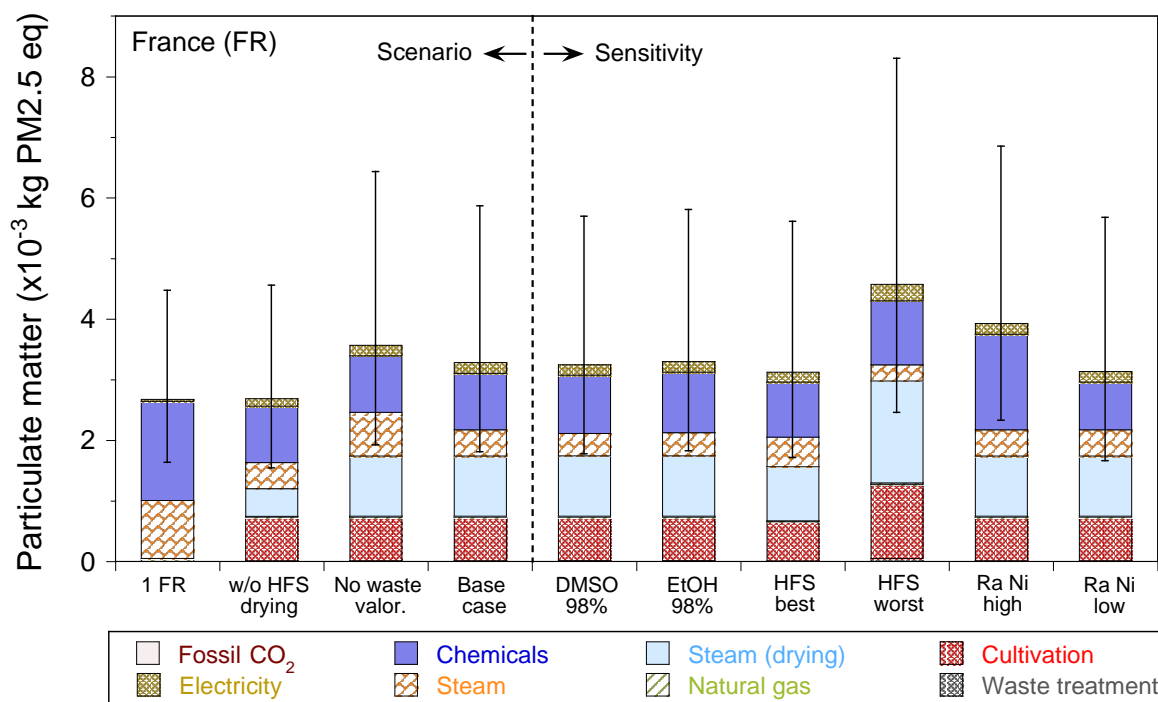


Fig. S14. Influence of HMDA production scenarios (left) and process variables (right) on particulate matter (midpoint category 3) for biobased route 3P FR vs. 1 FR. The error bars were estimated using the Monte Carlo tool available in SimaPro software.

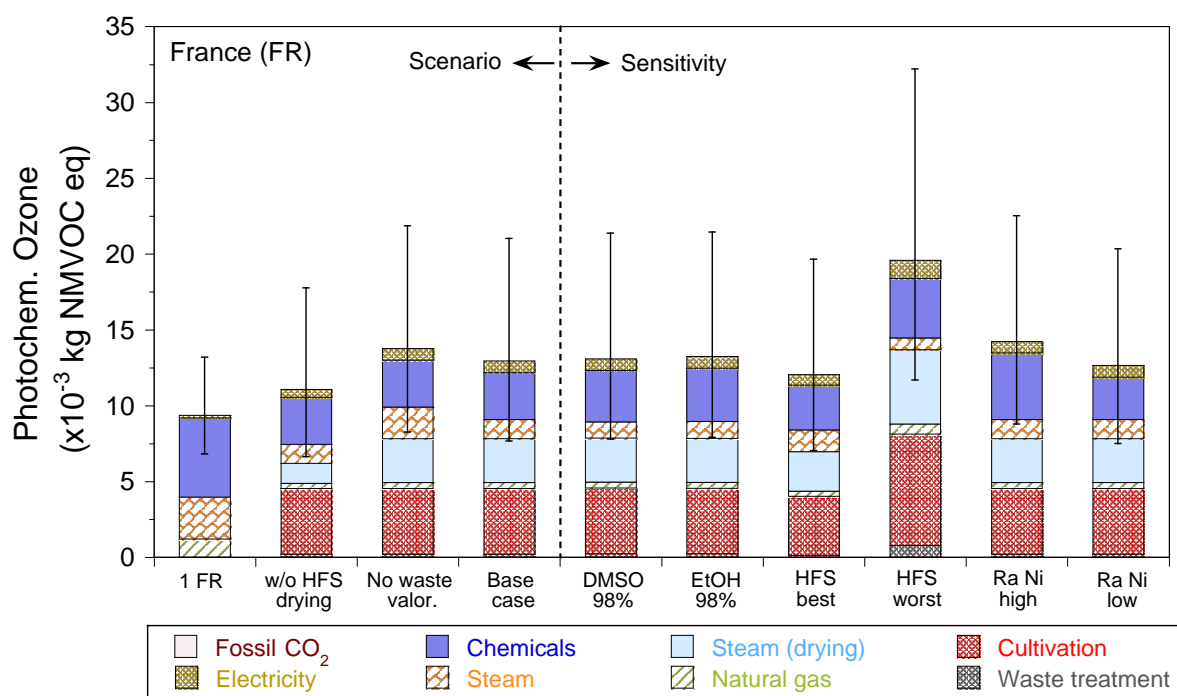


Fig. S15. Influence of HMDA production scenarios (left) and process variables (right) variables on photochemical ozone formation (midpoint category 4) for biobased route 3P FR vs. 1 FR. The error bars were estimated using the Monte Carlo tool available in SimaPro software.

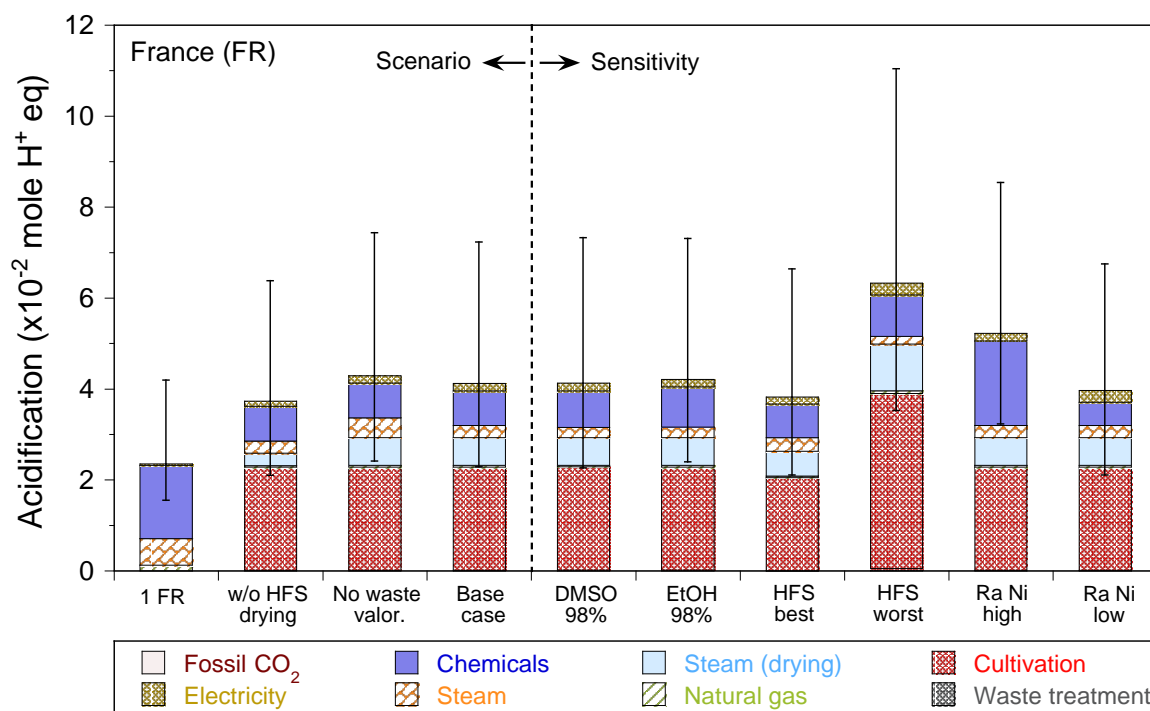


Fig. S16. Influence of HMDA production scenarios (left) and process variables (right) variables on acidification (midpoint category 5) for biobased route 3P FR vs. 1 FR. The error bars were estimated using the Monte Carlo tool available in SimaPro software.

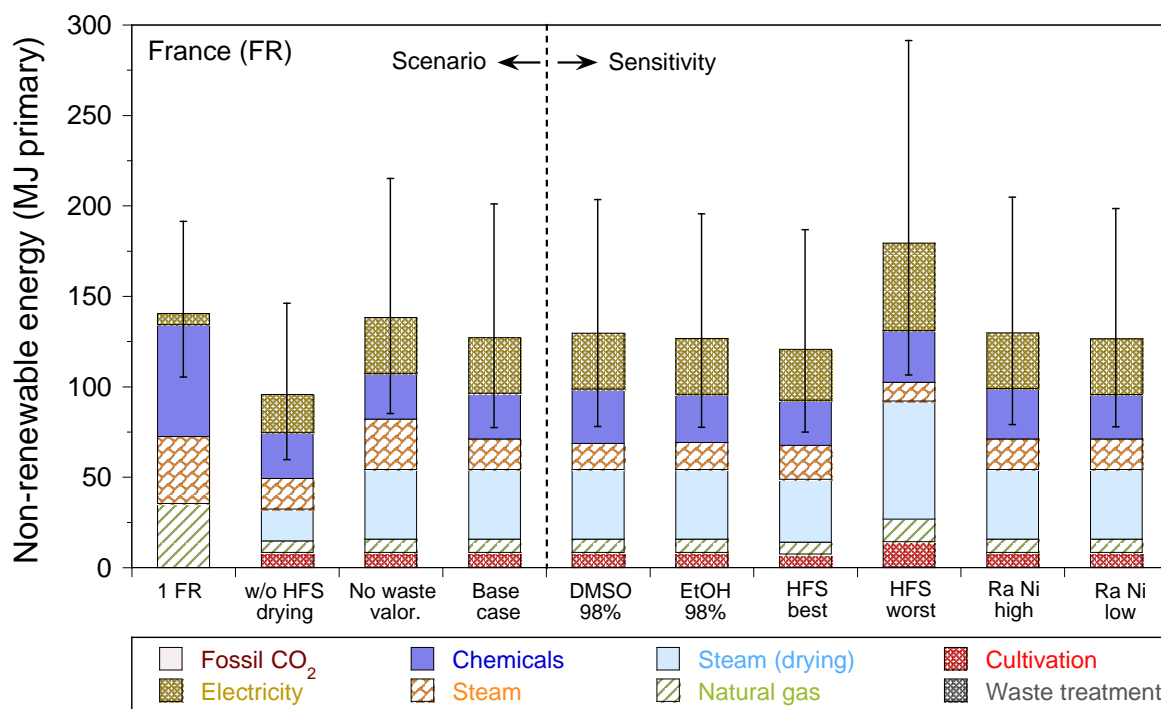


Fig. S17. Influence of HMDA production scenarios (left) and process variables (right) variables on non-renewable energy (midpoint category 9) for biobased route 3P FR vs. 1 FR. The error bars were estimated using the Monte Carlo tool available in SimaPro software.

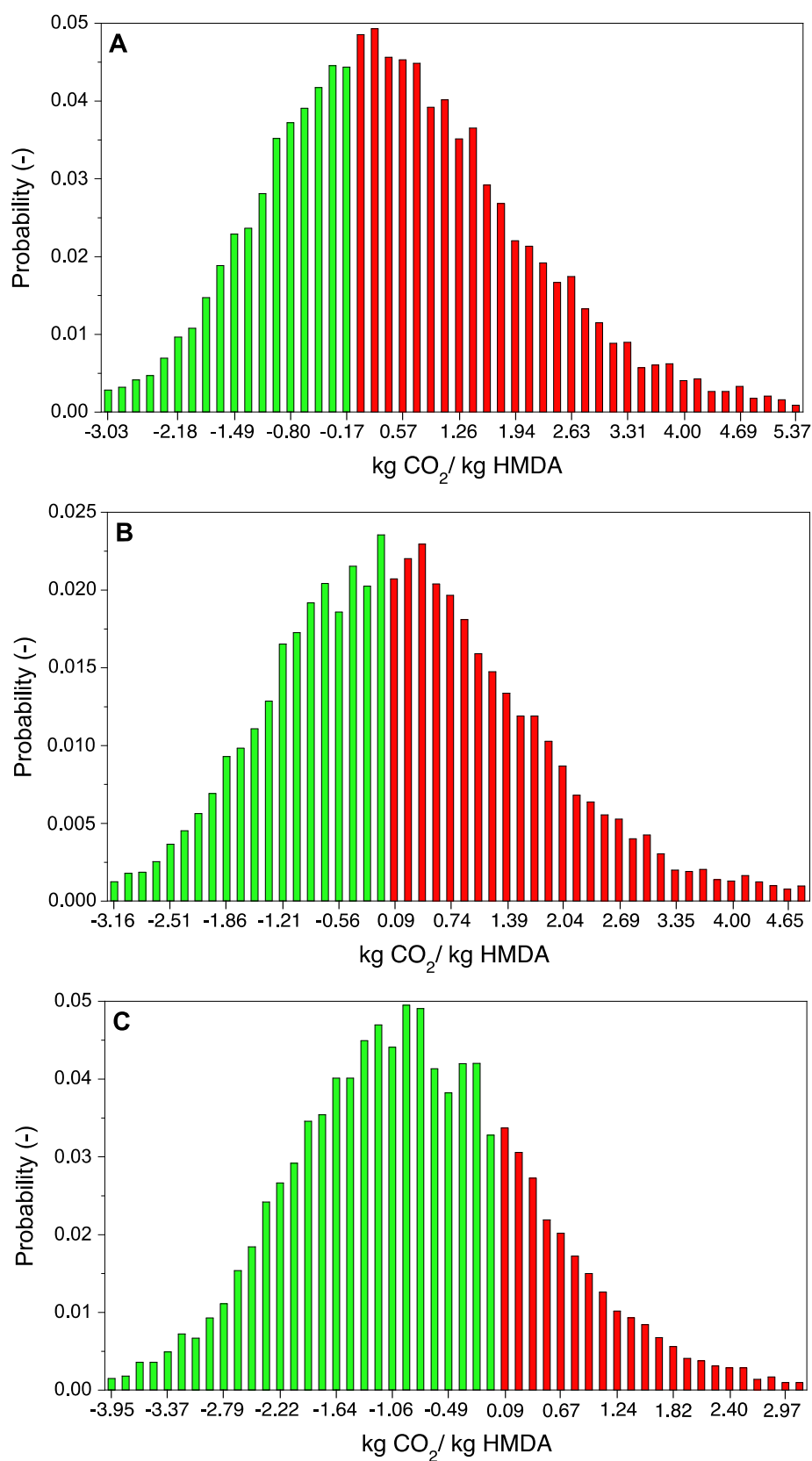


Fig. S18. Log-normal plots issued from Monte Carlo analysis for climate change (w/o carbon sink) comparing routes 3P FR and 1 FR. Scenarios: A) Base case, B) HFS best, and C) w/o HFS drying. The green and red color correspond to routes 3P FR and 1FR, respectively.

Table S1. HMDA process inventory for the base case (see **Table 1** in main text) for the routes (1) to (4) and for the intermediates: HCN (1), 1,6 HDO (2), THDFM (3), DFF (4), AM-THF (3) and AM-THF (4). Consumptions (or generations) are indicated for the raw materials, by-products and wastes in kg/kg product, for the catalysts in g/kg product and for the utilities in their respective units per kg of product (i.e. HMDA or above-mentioned intermediates). Prices of raw materials and by-products are indicated with their bibliographic references.

Inventory	Items and their unit	€/unit	Reference	HMDA BD (1)	HMDA (2)	HMDA (3)	HMDA (4)	HCN (1)	HMF (2,3,4)	1,6 HDO (2)	THDFM (3)	DFF (4)	AM-THF (3)	AM-THF (4)
Raw Materials	A ₁ Butadiene, kg	1.15	(a)	0.545	-	-	-	-	-	-	-	-	-	-
	A ₂ Nat. gas, kWh	0.027	(b)	8.86	-	-	-	16.32	-	-	-	-	-	-
	A ₃ Phosphoric acid, kg	1.15	(c)	0.005	-	-	-	0.010	-	-	-	-	-	-
	A ₄ Dry HFCS42%, kg	0.49	(d)	-	2.398	2.083	2.083	-	1.710	2.122	1.632	1.738	1.841	1.841
	A ₅ Ammonia, kg	0.46	(e)	0.409	0.293	0.296	0.296	0.750	-	-	-	-	0.262	0.262
	A ₆ Dihydrogen, kg	1.92	(f)	0.067	0.115	0.098	0.105	-	-	0.099	0.046	-	0.055	0.062
	A ₇ DMSO, kg	1.31	(c)	-	0.006	0.005	0.005	-	0.004	0.006	0.004	0.005	0.005	0.005
	A ₈ Hydrogen iodide, kg	42.65	(g)	-	-	0.001	0.001	-	-	-	-	-	-	-
	A ₉ Sodium bisulfite, kg	0.33	(h)	0.109	-	-	-	-	-	-	-	-	-	-
	A ₁₀ Sodium sulfite, kg	0.29	(h)	0.067	-	-	-	-	-	-	-	-	-	-
	A ₁₁ Ethanol, kg	0.95	(i)	-	0.003	0.003	-	-	-	0.003	0.002	-	0.003	-
	A ₁₂ Dichloromethane, kg	0.40	(c)	-	-	-	0.010	-	-	-	-	0.008	-	0.009
	A ₁₃ Dioxygen, kg	0.07	(j)	-	-	-	0.155	-	-	-	-	0.129	-	0.137
Catalysts	A ₁₄ Raney Nickel, g	-	F.D.	-	2.1	2.4	1.1	-	-	1.0	1.0	-	2.1	1.0
	A ₁₅ Cu(NTF ₂) ₂ , g	-	F.D.	-	2.2	1.9	1.9	-	1.5	1.9	1.5	1.6	1.7	1.7
	A ₁₆ Fe based, g	0.008	(h)	6.0	-	-	-	-	-	-	-	-	-	-
	A ₁₇ Pd/SiO ₂ , g	0.750	(k)	-	-	0.1	0.1	-	-	-	-	-	-	-
	A ₁₈ Rh-Re/SiO ₂ , g	2.179	(l)	-	0.1	-	-	-	-	0.1	-	-	-	-
	A ₁₉ Nafion resin, g	0.019	(m)	-	0.1	-	-	-	-	0.1	-	-	-	-
	A ₂₀ MnO ₂ , g	0.002	(c)	-	-	-	2.4	-	-	-	-	2.0	-	2.1
By-products	A ₂₁ Heavy amines, kg	0.65	(h)	0.013	-	-	-	-	-	-	-	-	-	-
	A ₂₂ Hexamethyleneimine, kg	4.25	(h)	0.004	-	-	-	-	-	-	-	-	-	-
Utilities	A ₂₃ Electricity, kWh	-	F.D.	0.46	0.52	0.46	0.45	0.19	0.10	0.32	0.20	0.20	0.32	0.31
	A ₂₄ Cooling water, m ³	-	F.D.	0.67	-	-	-	0.50	-	-	-	-	-	-
	A ₂₅ Natural gas, kWh	0.027	(b)	0.05	-	-	-	-	-	-	-	-	-	-
	A ₂₆ Steam, kg	-	F.D.	8.99	9.77	6.79	8.34	0.97	2.48	7.52	3.80	5.36	5.37	6.75
	A ₂₇ Process water, L	-	F.D.	1.44	-	-	-	0.39	-	-	-	-	-	-
	A ₂₈ Inert gas, L	-	F.D.	0.01	-	-	-	-	-	-	-	-	-	-
	A ₂₉ Steam credit for waste valorization, kg	-	F.D.	-	4.43	2.70	2.61	-	1.20	2.94	1.16	1.22	2.29	2.20
Wastes	A ₃₀ Incineration of organic wastes, kg	-	F.D.	-	0.70	0.49	0.48	-	0.29	0.52	0.28	0.29	0.42	0.41
	A ₃₁ Fossil CO ₂ from process, kg	-	(n)	0.616	-	-	-	1.14	-	-	-	-	-	-
	A ₃₂ Fossil CO ₂ from waste incineration, kg	-	(n)	ND	0.013	0.012	0.006	N.D.	0.005	0.012	0.009	0.005	0.011	0.005
	A ₃₃ Biogenic CO ₂ from waste incineration, kg	-	(n)	0	0.928	0.788	0.772	0	0.413	0.634	0.394	0.420	0.673	0.659

F.D. refers to factory data; N.D.: no data; (a) Butadiene Europe Spot fob, March 2013 (ref.¹⁸); (b) Natural gas trading, March 2013 (ref.¹⁹); (c) Export price from China, March 2013 (ref.²⁰); (d) Milling & Baking News, US Midwest spot price HFCS 42% on dry weight basis (ref.²¹); (e) Ammonia Europe Spot cfr, March 2013 (ref.¹⁸); (f) Hydrogen price estimated from methane's one using Solvay methodology; (g) Iodide cif price average 2012 (ref.²²); (h) PEP yearbook 2012 (ref.²³); (i) Ethanol-96% Domestic FD Germany, March 2013 (ref.¹⁸); (j) Oxygen price on e-gas.cn in February 2013 (ref.²⁴); (k) Catalyst composition : 5%w/w Pd; 95%w/w SiO₂, catalyst price estimated in €/gram as 5%×(price Pd), given market prices of Pd at 15 €/gram at end 2012 (ref.²⁵); (l) Catalyst composition : 6%w/w Re; 6.5% w/w Rh; 87.5% SiO₂, catalyst price estimated in €/gram as 6%×(price Re)+6.5%×(price Rh), given market prices of Rh at 30.9 €/gram and Re at 2.8 €/gram at end 2012 (ref.²⁵); (m) Nafion NR50 polymer beads at end 2012 (ref.²⁶); (n) CO₂ emissions calculated from mass balance.

Table S2. Process inventory of HFS production (kg / kg of dry HFS, base case) from starch made from corn or potato

Inventory	Items and their unit		HFS from potato starch, 20%	HFS from corn starch, 14%
Raw Materials	A ₃₄	Starch, kg	1.250	1.163
	A ₃₅	Activated carbon, g	0.483	0.483
	A ₃₆	Caustic soda 50%, kg	0.012	0.012
	A ₃₇	Enzymes, g	2.234	2.234
	A ₃₈	Magnesium sulfate .7H ₂ O, g	0.193	0.193
	A ₃₉	Sulfuric acid, kg	0.011	0.011
Utilities	A ₄₀	Natural gas, kWh	0.18	0.18
	A ₄₁	Electricity, kWh	0.82	0.82
	A ₄₂	Steam, kg	4.51	4.51

A₃₄₋₄₂: after data of the PEP yearbook 2012 (ref. ²⁷).

Table S3. Molar yield for the reaction of HFS to HMF from values indicated in literature

Yields	Min	Base	Max
Fructose → HMF	87%	87%	97%
Glucose → HMF	22%	81%	81%
Global yield	49%	83.5%	88%

Table S4. Physicochemical properties of the main chemicals considered for the bio-routes

Chemical	T (°C)	P (atm)	Specific heat (J.g ⁻¹ .°C ⁻¹)	Enthalpy of vapor. (kJ/kg)	Boiling T (°C)	Enthalpy of fusion (kJ/kg)	Melting T (°C)	Density (g/cm ³)	M _w (g/mol)
HMF	25	1	2.05	661.3	291.5	157.0	32.0	1.29	126.11
1,5-HDO	25	7.10 ⁻⁴	-	-	89.0	-	-	0.98	118.17
1,6-HDO	42	1	2.88	702.2	252.8	215.5	42.0	0.96	118.17
DFF	25	1	-	415.3	276.8	-	110.0	1.30	124.09
α-D-Glucose	25	1	1.99	923.8	343.9	174.3	146.0	1.54	180.16
D-Fructose	25	1	-	-	-	168.2	103.0	1.69	180.16
AM-THF	25	1	-	-	227.8	-	-	1.01	130.19
HMDA	41	1	1.98	452.7	199.9	347.06	40.8	0.85	116.20
DMSO	25	1	1.96	683.4	190.9	178.1	18.5	1.10	78.13
Dichloromethane	25	1	1.19	343.6	39.8	54.1	-95.1	1.32	84.93
Cyclohexane	25	1	1.83	359.0	80.7	32.5	6.5	0.77	84.16
Ethanol	25	1	2.43	922.5	78.3	106.9	-114.1	0.79	46.07
Water	25	1	4.18	2431.9	100.0	332.7	0.0	0.99	18.01

Table S5. Pedigree matrix with the scores used to assess the quality of data sources (readapted from ref.²⁸)

Score	1	2	3	4	5
U1 Reliability	Verified data based on measurements	Verified data partly based on assumptions or non-verified data based on measurements	Non-verified data partly based on qualified estimates	Qualified estimate (<i>e.g.</i> , by industrial expert)	Non-qualified estimate
	1.00	1.05	1.10	1.20	1.50
U2 Completeness	Representative data from all sites relevant for market considered over adequate period to even out normal fluctuations	Representative data from >50% of sites relevant for market considered over adequate period to even out normal fluctuations	Representative data from only some relevant sites (<<50%) or >50% of sites but from shorter periods	Representative data from only one relevant site or some sites but from shorter periods	Representativeness unknown or data from a small number of sites and shorter periods
	1.00	1.02	1.05	1.10	1.20
U3 Temporal correlation	< 3 years difference to time period of the dataset	<6 years difference to time period of the dataset	<10 years difference to time period of the dataset	<15 years difference to time period of the dataset	Age of data unknown or >15 years difference to time period of the dataset
	1.00	1.03	1.10	1.20	1.50
U4 Geographical correlation	Data from area under study	Average data from larger area in which the area under study is included	Data from area with similar production conditions	Data from area with slightly similar production conditions	Data from unknown or distinctly different area
	1.00	1.01	1.02	1.05	1.10
U5 Further technological correlation	Data from enterprises, processes and materials under study	Data from processes/materials under study but from different enterprises	Data from processes/materials under study but different technology	Data on related processes or materials	Data on related processes on laboratory scale or from different technology
	1.00	1.05	1.20	1.50	2.00

Table S6. Scores used for the Pedigree matrix to assess the quality of data sources (derived from ref.²⁸)

Route	Reaction	U1	U2	U3	U4	U5	U6*	SD ²
1FR	CH ₄ + NH ₃ → HCN	2	3	5	5	1	N.D.	1.53
	BD + HCN → HMDA	2	3	5	5	1	N.D.	1.53
3P FR	Starch → HFS	2	4	5	3	2	N.D.	1.53
	HFS → HMF	2	4	3	3	2	N.D.	1.17
	HMF → THFDM	2	4	1	3	2	N.D.	1.14
	THFDM → AM-THF	2	4	2	3	2	N.D.	1.53
	AM-THF → HMDA	2	4	1	3	2	N.D.	1.14

* Sample size factor: considered as an obsolete indicator and was left unspecified in the matrix

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