

Supporting information

Greener ring opening of epoxidized methyl oleate using novel acid functionalized iron nanoparticle catalyst

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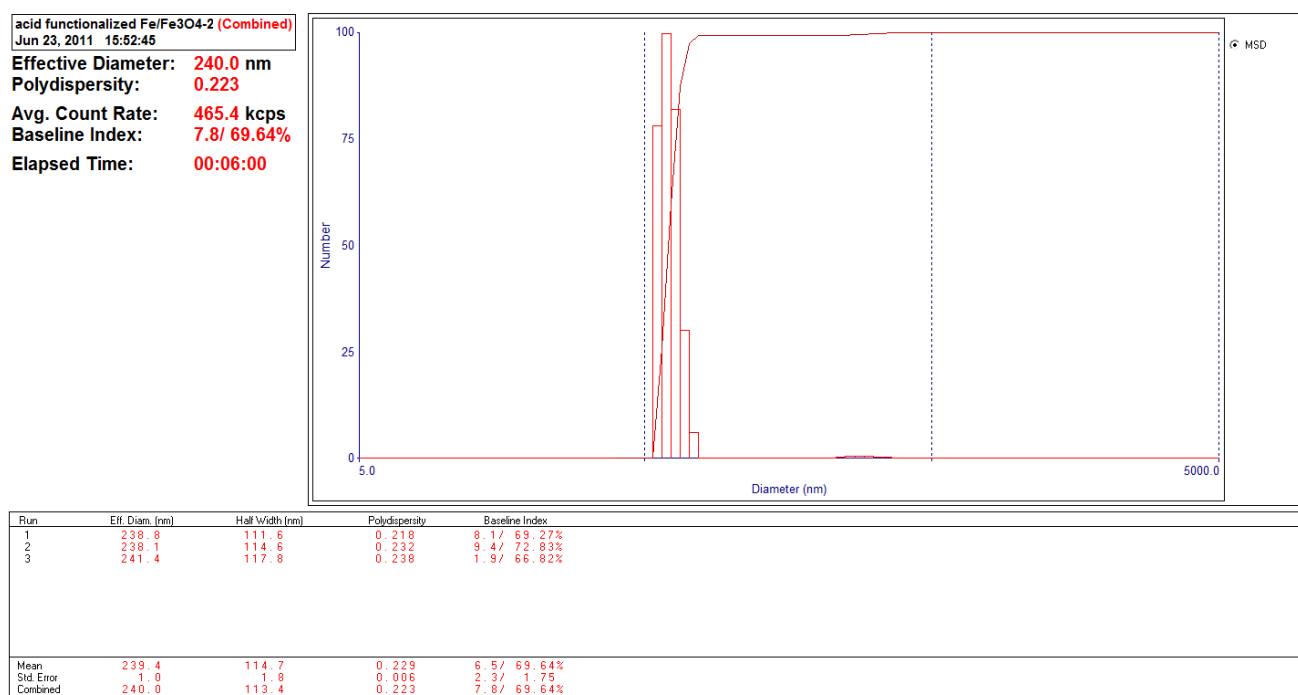


Figure S1. Dynamic Light Scattering measurement of the sulfamic acid functionalized core/shell Fe/Fe₃O₄ nanoparticles

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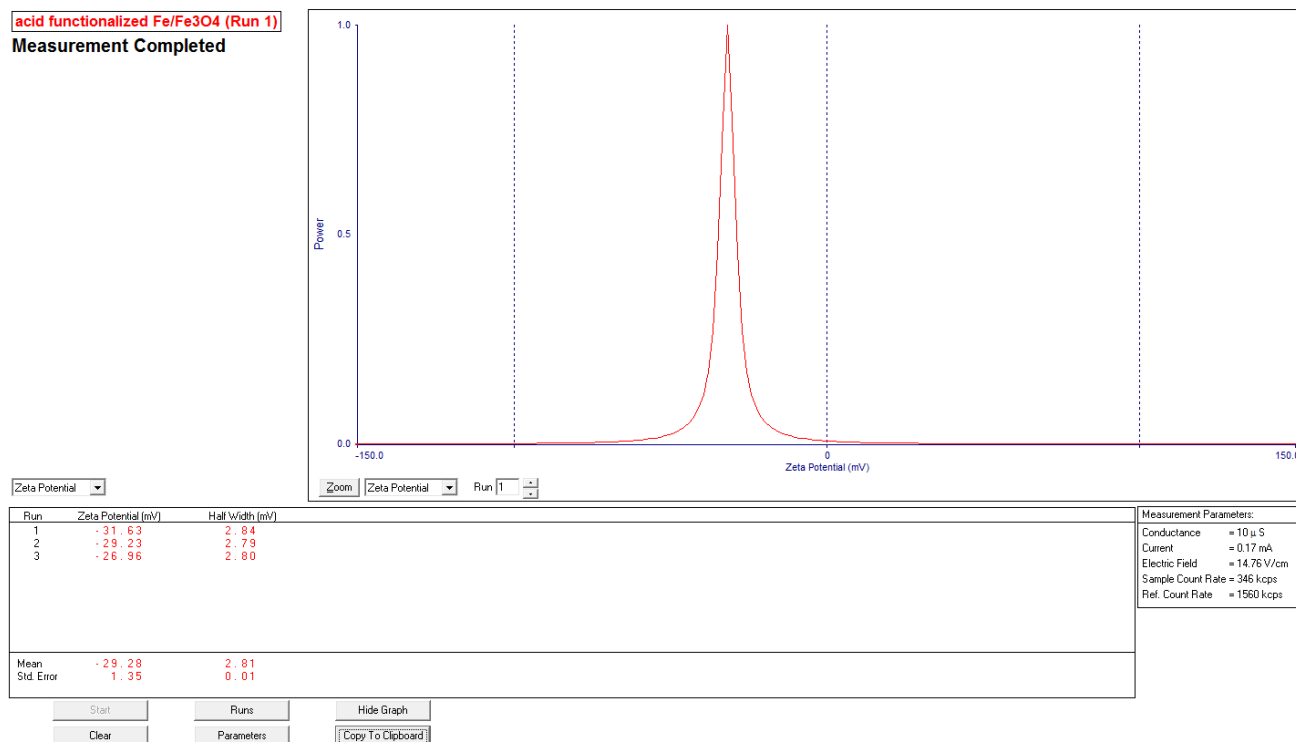


Figure S2. Zeta potential of the sulfamic acid functionalized core/shell Fe/Fe₃O₄ nanoparticles

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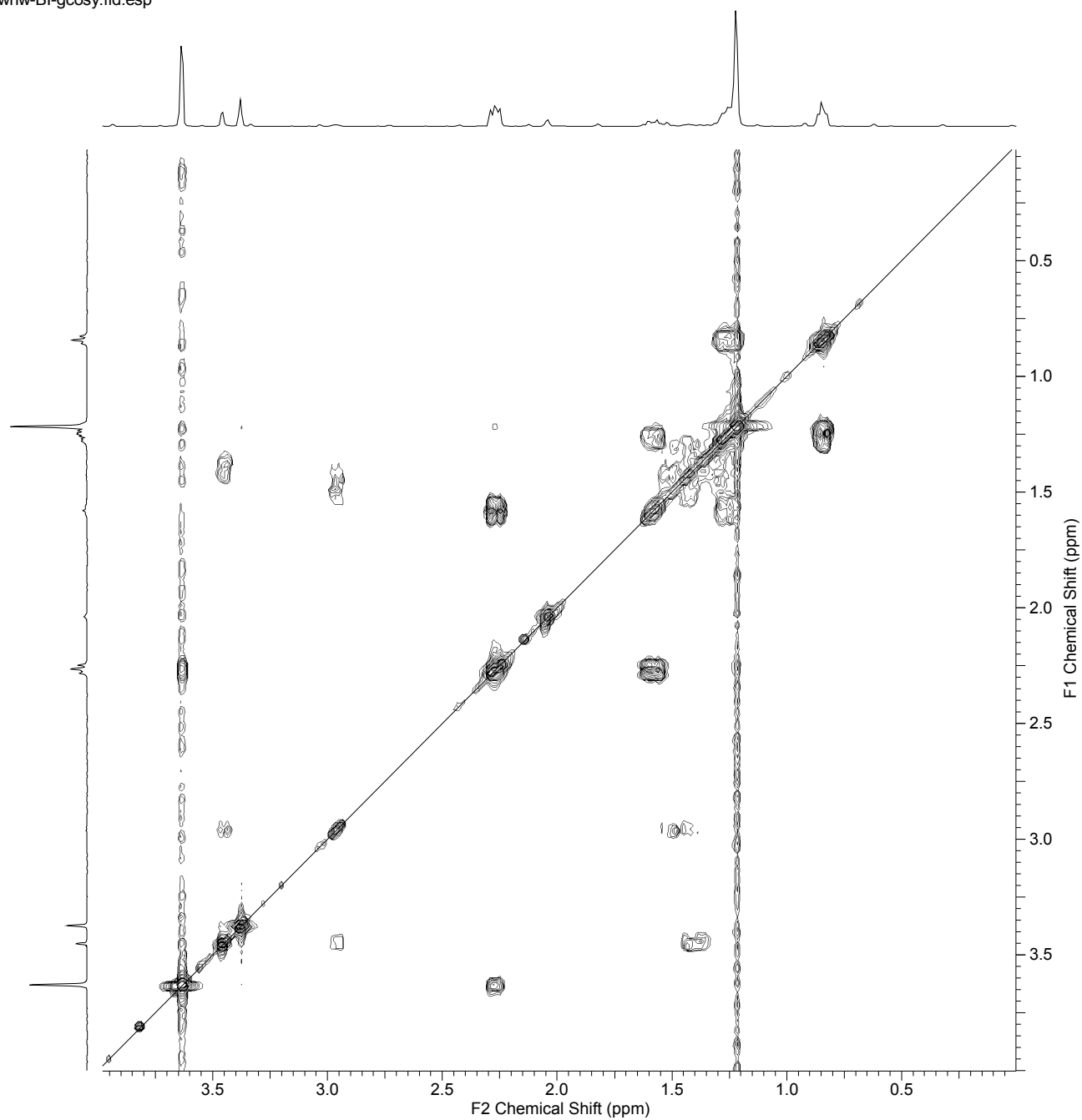


Figure S3. ^1H - ^1H COSY NMR of α -methoxy-hydroxylation of EMO by the sulfamic acid-functionalized Fe/Fe₃O₄ NPs

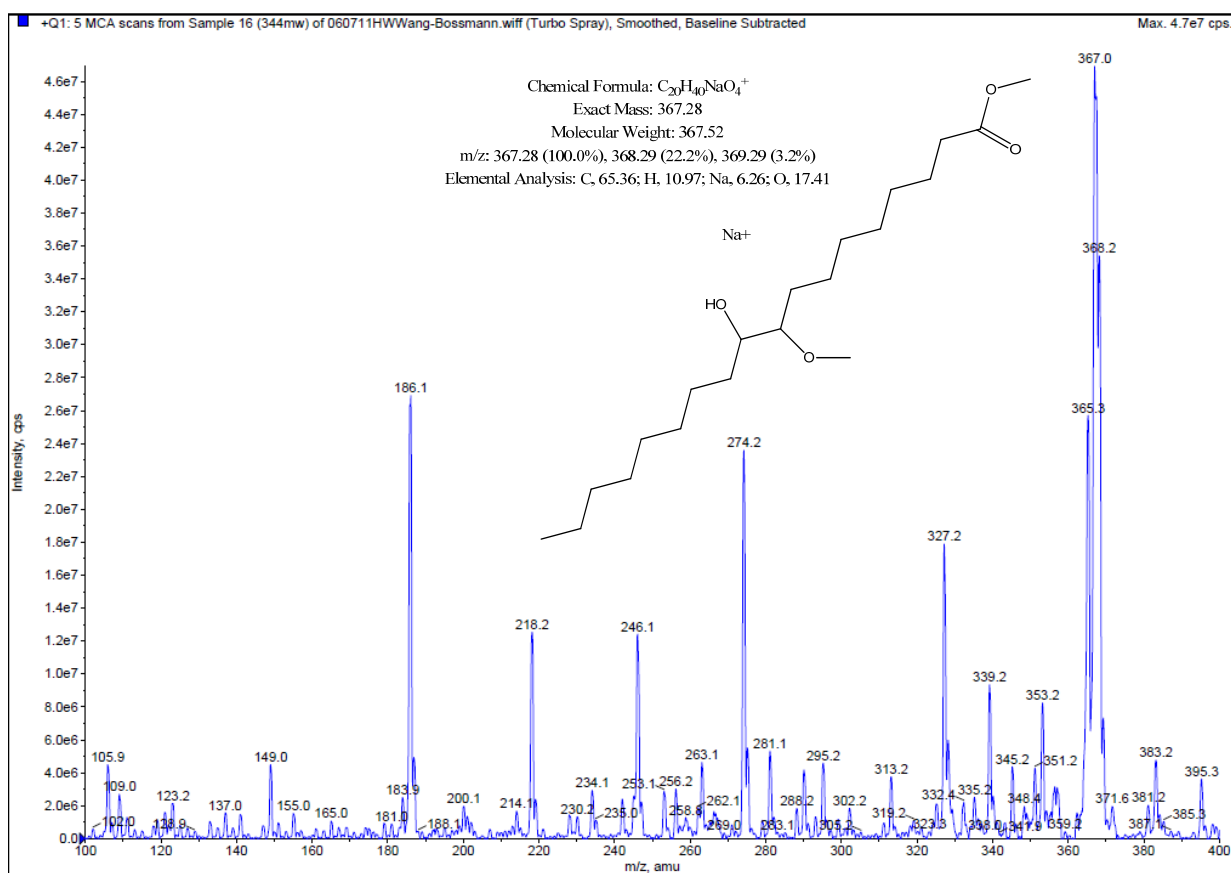
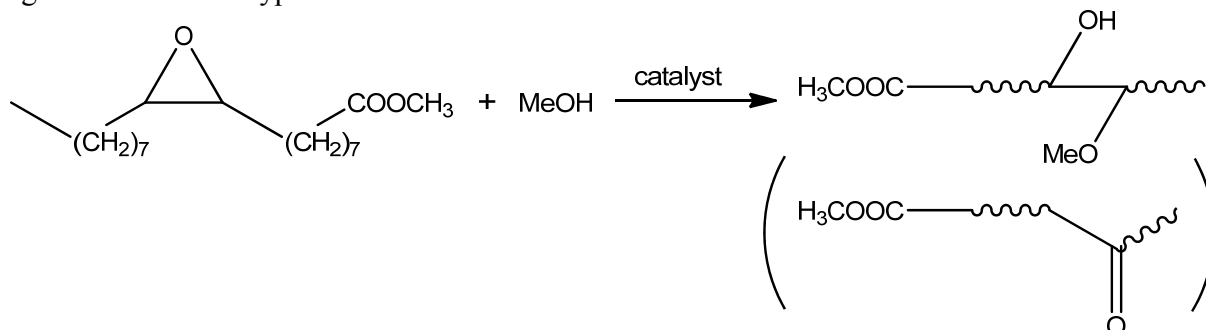


Figure S4. ESI-MS of α -methoxy-hydroxylation of EMO by the sulfamic acid-functionalized Fe/Fe₃O₄ NPs

Synthetic Routes

Four routes for the following ring-opening of epoxidized methyl oleate (EMO) were compared on a 1 kg scale. A ketone byproduct seen in two of the routes studied is shown in brackets.



1) Iron Nanoparticle Method

Materials:

EMO 0.907 kg (2.90 mol)
sulfonated iron nanoparticles 90 g
MeOH 0.930 kg (29.0 mol)

Procedure:

Stir for 30 min at 40 °C. Remove remaining MeOH via distillation. Yield: 100%

Products/Residuals:

Ring-opened EMO 1.00 kg (product)
Sulfonated iron nanoparticles 90 g (100% recycled)
MeOH 0.837 kg (recycled)

2) Sulfuric Acid Method

Materials:

EMO 0.907 kg (2.90 mol)
H₂SO₄ 90 g
MeOH 0.930 kg (29.0 mol)

Procedure:

Stir for 30 min at room temperature. Remove remaining MeOH via distillation. Yield: 100%

Products/Residuals:

Ring-opened EMO 1.00 kg (product)
H₂SO₄ 90 g (not recycled)
MeOH 0.837 kg (recycled)

3) SAC13 Resin Method

Materials:

EMO 1.09 kg (3.50 mol)

SAC 13 (commercial recyclable heterogeneous sulfonic acid functionalized resin) 90 g
MeOH 1.12 kg (35.0 mol)

Procedure:

Stir for 60 min at 60 °C. Remove remaining MeOH via distillation. Yield: 83%

Products/Residuals:

Ring-opened EMO 1.00 kg (product)
SAC 13 90 g (recycled, cleanup not considered in LCA)
MeOH 1.03 kg (recycled)
Ketone byproduct 0.19 kg (0.59 mol)

4) Amberlyst-15 Resin Method

Materials:

EMO 1.04 kg (3.34 mol)
Amberlyst-15 (commercial recyclable heterogeneous sulfonic acid functionalized resin) 0.020g
MeOH 1.07 kg (33.4 mol)
Ketone byproduct 0.14 kg (0.43 mol)

Procedure:

Stir for 100 min at 60 °C. Remove remaining MeOH via distillation. Yield: 87%

Products/Residuals:

Ring-opened EMO 1 kg (product)
Amberlyst-15 90 g (recycled, cleanup not considered in LCA)
MeOH 0.98 kg (recycled)

Impact assessment method

The reaction impact assessment for epoxide ring opening was carried out using a procedure based on the ISO life-cycle assessment method^{1,2}. This approach includes both the amount of waste as well as the harmfulness of the waste. Our procedure was adapted from Mercer and coworkers' exercise in impact assessment "Choosing the Greenest Synthesis"³. We compare four reactions with respect to 9 environmental risks. For most of these risks, the chemical outputs are compared to reference chemicals; this allows addition of all contributors to the risk for comparison within a synthetic route as well as between routes. In our assessment, we built a multimedia compartmental model (MCM) to assess the partitioning behavior of each chemical into four environmental compartments (air, water, soil & sediment). This was implemented in assessing the human toxicity risk of each procedure.

Assumptions for Impact Assessment

- We assume 100% recovery of all recyclable catalysts (NPs, SAC13, Amberlyst-15); in reality recovery of NPs would likely be less involved than recovery of the resins, due to the innovative use of a magnet.
- We assume 100% environmental loss of H₂SO₄ in method 2, as it cannot be reused.
- We assume each reaction cools and is worked up prior to solvent distillation.
- We assume 0.1% environmental loss of MeOH in all procedures, which would likely occur during distillation.
- We assume 0.1% environmental loss of ketone byproduct⁴ (where yields are less than 100%). The remaining byproduct material is incinerated. Although the literature suggests oligomeric byproducts occur in addition to the ketone byproduct, these have similar reactivity but are more complex to characterize. Despite this simplification, commentary on alternate byproducts appears throughout this assessment.

- All four routes were scaled in a linear fashion (i.e. material quantities and yields) to produce 1 kg or product for even comparison.
- Because all four routes produce the same mass of product, the environmental impact of the product itself was ignored.

The Nine Factors

1) Acidification Potential

As none of the four processes involve the use or production of gases, their contribution to acid rain is not significant. All acidification potential indices (I_{AP}) were, therefore, zero.

2) Ozone Depletion Potential

As none of the four processes involve the use of halogenated solvents or materials, they do not contribute to stratospheric ozone depletion. All ozone depletion potential indices (I_{OD}) were, therefore, zero.

3) Smog Formation Potential

Methanol escape from all four processes was considered for smog formation potential. Although byproduct in processes 3 and 4 could participate in smog formation, it is non-volatile. A smog formation potential (SFP_i) was determined by comparing methanol's maximum incremental reactivity (MIR_i) to that of a standard mixture of reference organic gases (MIR_{ROG}). The SFP_i is expressed as the mass (kg) ozone formed per mass (kg) of chemical released. Ozone is used as the reference compound as it is a significant participant in photochemical smog.

A smog formation potential index I_{SF} (in equivalent kg of ozone) was calculated for each process, based on the contribution from methanol released into the environment. Had other species contributed, they would have been included here.

$$I_{SF} = \sum_i SFP_i \cdot m_i = SFP_{MeOH} \cdot m_{MeOH} = 0.16 \cdot m_{MeOH}$$

	Route			
	1	2	3	4
SFP_{MeOH}	0.16	0.16	0.16	0.16
m_{MeOH} (kg MeOH)	9.30×10^{-4}	9.30×10^{-4}	1.12×10^{-3}	1.07×10^{-3}
I_{SF} (kg ozone)	1.49×10^{-4}	1.49×10^{-4}	1.79×10^{-4}	1.71×10^{-4}

SFP for methanol was taken from Guinée *et al.*¹.

4) Global Warming Potential

The contribution of each process to global warming potential included three components: firstly, the global warming potential of escaped volatiles (in all cases MeOH) over time compared with an equal mass of atmospheric CO_2 ; secondly, the amount of CO_2 produced to create the energy used in heating and distillation; thirdly, the CO_2 produced by incineration of the organic byproduct.

Global warming potential of escaped MeOH, based on a 100-year time horizon was calculated in a similar manner to the smog formation potential.

$$I_{GWP} = \sum_i GWP_i \cdot m_i = GWP_{MeOH} \cdot m_{MeOH} = 2.8 \cdot m_{MeOH}$$

CO₂ emissions from heating were calculated assuming heating from room temperature (20°C) to reaction temperature or distillation temperature. C_{p,i} represents the gravimetric heat capacity of species i, while q is the heat required to increase i's temperature by the stated difference. As no gravimetric heat capacity was available for EMO, it was estimated based on that of *cis*-9-octadecenoic acid (C₁₈H₃₄O₂) of 2.043 J/g/K. This assumption is reasonable for heating, as molecular composition and mass is similar. A sample calculation is given for methanol in route 1:

$$q_i = m_i \cdot C_{p,i} \cdot (T_{rxn} - T_{ambient})$$

$$q_{MeOH} = 0.930 \text{ kg} \cdot 2.531 \text{ kJ/kg/K} \cdot (40 - 20) \text{ K} = 47.1 \text{ kJ}$$

Distillation of methanol was calculated in a similar manner to the above, with the addition of the heat required for distillation (ΔH_{vap}). Again, a sample calculation for route 1:

$$q_i = [m_i \cdot C_{p,i} \cdot (T_{boiling} - T_{ambient})] + [m_i \cdot \Delta H_{vap,i}]$$

$$q_{MeOH} = [0.837 \text{ kg} \cdot 2.531 \text{ kJ/kg/K} \cdot (65 - 20) \text{ K}] + [0.837 \text{ kg} \cdot 1213 \text{ kJ/kg}] = 1190 \text{ kJ}$$

The heat required to perform the reaction and heat required to distill methanol were combined (q_{tot}) so the equivalent mass of CO₂ from heating could be determined. For every kilojoule of heat required, $4.2 \cdot 10^{-5}$ kg CO₂ is produced.

$$m_{CO_2} = q_{tot} \cdot 4.2 \cdot 10^{-5} \text{ kg/kJ}$$

Finally, the CO₂ released by combustion of the ketone byproduct of reactions 3 and 4 was calculated. NC designates the number of carbons in each molecule, because each carbon atom would form one CO₂ equivalent after ideal combustion. As we saw previously, this is later multiplied by the mass of byproduct burned after each reaction.

$$GWP_i = \frac{NC_i/MW_i}{NC_{CO_2}/MW_{CO_2}} = \frac{18/312.49}{1/44.01} = 2.54$$

The global warming potentials from all three calculations were added to determine the total GWP index for each route.

	Route			
	1	2	3	4
MeOH release (kg CO ₂)	2.60×10^{-3}	2.60×10^{-3}	3.14×10^{-3}	2.99×10^{-3}
Energy requirements for heating (kg CO ₂)	5.02×10^{-2}	4.66×10^{-2}	6.58×10^{-2}	6.25×10^{-2}
CO ₂ from byproduct combustion (kg CO ₂)	0	0	4.71×10^{-4}	3.44×10^{-4}
Total I _{GWP} (kg CO ₂)	5.28×10^{-2}	4.92×10^{-2}	6.94×10^{-2}	6.58×10^{-2}

GWP for methanol was taken from Forster *et al.*⁵. Heat capacities were taken from the CRC Handbook⁶. CO₂ to kJ conversion was based on the estimate of Stageland *et al.*⁷.

5) Human Toxicity Potential (inhalation)

For assessment of inhalation and ingestion toxicity the MCM was used, based on parameters set out by Mercer et al. Environmental compartments were assigned representative properties, as follows:

Compartment	Volume, V (m ³)	Density, d (t/m ³)	Fraction organic material, ϕ
Air	1.0×10 ¹⁰	N/A	N/A
Water	7.0×10 ⁶	N/A	N/A
Soil	9.0×10 ³	1.5	0.02
Sediment	2.0×10 ⁴	1.5	0.04

Equilibrium partitioning was assumed between the environmental compartments, according to the octanol-water partition coefficient (K_{ow}), organic carbon partition coefficient (K_{oc}), and Henry's law constant, H.

Chemical	K_{ow}	K_{oc}	H (atm·m ³ ·mol ⁻¹)
methanol	0.204	8.37×10 ⁻²	4.49×10 ⁻⁶
ketone byproduct	1.05×10 ⁸	4.29×10 ⁷	1.99×10 ⁻⁵
sulfuric acid	2.45×10 ⁻⁶	1.01×10 ⁻⁶	1.0×10 ⁻¹⁹
toluene	501	205	0.0067

Above, K_{oc} has been calculated from K_{ow} using the formula:

$$K_{oc} = 0.41 \cdot K_{ow}$$

An arbitrary mass of each chemical emitted was compared to an equal mass of toluene, yielding these relative concentrations:

Chemical	Air (C_i/C_{tol})	Water (C_i/C_{tol})	Soil (C_i/C_{tol})	Sediment (C_i/C_{tol})
methanol	5.99×10 ⁻¹	8.94×10 ⁻²	3.64×10 ⁻¹	3.64×10 ⁻¹
ketone byproduct	3.81×10 ⁻⁵	1.28×10 ⁻²	2.68×10 ³	2.68×10 ³
sulfuric acid	5.50×10 ⁻¹⁵	3.68×10 ⁻²	1.80×10 ⁻⁶	1.80×10 ⁻⁶
(toluene)	1.00	1.00	1.00	1.00

LC50's used in this model were as shown below. Unfortunately, no estimate was available for the ketone byproduct, so a very conservative estimate (100 ppm) was chosen. This worst case scenario was shown to have minimal effect on the overall INHTP for the reaction because the mass emitted is very low, and the percentage in the atmosphere is almost negligible. 4h LC50 values were used where available. The sulfuric acid LC50 is a 2h value but, based on the very low resultant INHTP, we assume that the 4h LC50 would result in a similarly negligible INHTP.

Chemical	LC50 (ppm)
methanol	64000
ketone byproduct	(100)
sulfuric acid	510
toluene	5400

By combining relative LC50's with relative concentrations in the air, the inhalation toxicity potential (INHTP) was found for each chemical, relative to an equal mass of toluene, by this equation:

$$INHTP = \frac{C_i(\text{air})}{C_{\text{tol}}(\text{air})} \times \frac{LC50_{\text{tol}}}{LC50_i}$$

Chemical	INHTP
methanol	5.05×10^{-2}
ketone byproduct	2.06×10^{-3}
sulfuric acid	5.8×10^{-14}
(toluene)	1.00

For all routes, the toxicity risk via inhalation was relatively low, as a result of non-volatile and relatively low-toxicity species. Methanol was volatile but its inhalation toxicity was low compared to the reference chemical, toluene. Sulfuric acid was insufficiently volatile to contribute to inhalation toxicity potential. Unfortunately, LC50 data was unavailable for the ketone byproduct; however, with a conservative assumption on toxicity of 1000 ppm, the low volatility and low emissions are sufficient to prevent this from posing an inhalation toxicity concern.

MCM parameters were suggested by Mercer and Jessop³. All K_{ow} values were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2011 ACD/Labs), by SciFinder. Methanol H was taken from Meylan and Howard⁸. Ketone byproduct H was estimated in ChemDraw, as per Mercer and Jessop's suggested procedure³. Toluene H was taken from Shiu and Ma⁹. Methanol LC50 was taken from the Sigma Aldrich MSDS for methanol¹⁰. Toluene LC50 was taken from Urrea-Bulla¹¹. Sulfuric Acid LC50 was taken from the Sigma Aldrich MSDS for sulfuric acid¹⁰.

6) Human Toxicity Potential (ingestion)

As with inhalation toxicity, ingestion toxicity was assessed with the use of our MCM. LD50's used in this model were as shown below:

Chemical	LD50 (mg/kg)
methanol	5628
ketone byproduct	3000
sulfuric acid	2140
toluene	5580

By combining relative LD50's with relative concentrations in the water (see section 5), the ingestion toxicity potential (INGTP) was found for each chemical, relative to an equal mass of toluene, by this equation:

$$INGTP = \frac{C_i(\text{water})}{C_{\text{tol}}(\text{water})} \times \frac{LD50_{\text{tol}}}{LD50_i}$$

Chemical	INGTP
methanol	886
ketone byproduct	2.39×10^{-2}
sulfuric acid	961
(toluene)	1.00

The sulfuric acid partitioning into water caused dramatic ingestion toxicity associated with route 2. In routes 3 and 4, the ketone byproduct caused very slight toxicity compared with methanol emissions. This results from the hydrophobic byproduct's affinity for soil and sediment compartments. Although the LD50 for the ketone byproduct is unknown, it was approximated using a shorter-chain ketone/methyl ester: methyl 3-oxobutanoate. This approximation is not ideal, due to lower bioaccumulation of the smaller species; however, since ingestion toxicity is estimated on a mass basis, the lower molecular weight would compensate for this difference to some extent.

Methanol LD50 was taken from Larionov, relying on SciFinder's translation from Russian¹². Sulfuric acid LD50 was the Sigma Aldrich MSDS for sulfuric acid¹⁰. Toluene LD50 was taken from Isayev¹³. Methyl 3-oxobutanoate LD50 was taken from Smyth¹⁴.

7) Persistence

Methanol's atmospheric half-life was calculated based on Kwok and Atkinson's method at 298K. First the rate of H abstraction is calculated (increased by the electron donating hydroxyl group). Then the half-life is calculated based on an assumed OH radical concentration of $10^6 \text{ molec cm}^{-3}$

$$k_{H \text{ abstraction}} = k_{\text{prim}} \cdot F(X) = k_{\text{prim}} \cdot F(OH) = 1.36 \cdot 10^{-12} \text{ cm}^2 \text{ molec}^{-1} \text{ s}^{-1} * 3.5 \\ = 4.77 \cdot 10^{-12} \text{ cm}^2 \text{ molec}^{-1} \text{ s}^{-1}$$

$$t_{1/2} = \frac{1}{4.77 \cdot 10^{-12} \text{ cm}^2 \text{ molec}^{-1} \text{ s}^{-1} * 10^6 \text{ molec cm}^{-3}} = 2.1 \cdot 10^6 \text{ s} = 24 \text{ days}$$

As the ketone byproduct was much less volatile than methanol, its half-life was estimated via a Boethling index. With respect to aerobic biodegradation, the lifetime was estimated as follows, where a_n and f_n refer to constants associated with various functional groups and the number of such groups. The Boethling index of 2.9 indicates a lifetime on the order of weeks.

$$\text{Boethling index}(BI) = 3.199 - (0.00221 \cdot MW) + \sum a_n \cdot f_n$$

$$BI_{\text{byproduct}} = 3.199 - (0.00221 \cdot 312.49) + 0.298(\text{alkyl}) - 0.023(\text{ketone}) + 0.140(\text{ester}) = 2.9$$

Methanol atmospheric lifetime was estimated using the Kwok and Atkinson method¹⁵. The ketone byproduct lifetime was estimated using Boethling's index method¹⁶.

8) Bioaccumulation

In all syntheses the only species which would bioaccumulate appreciably is the ketone byproduct from reactions 3 and 4. Methanol is soluble in water, and its estimated bioconcentration factor is 1, therefore bioaccumulation does not occur. There is no data available for the ketone byproduct, but methyl oleate provides a reasonable model. Methyl oleate has an estimated bioconcentration factor of $7.3 \cdot 10^5$, and an estimated log P of 8.02, indicating very high bioaccumulation potential. This very hydrophobic nature is due to the large size, long alkyl chains and low polarity of the molecule. Sulfuric acid would not be expected to bioaccumulate.

Bioaccumulation potential was calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2011 ACD/Labs), as referenced by SciFinder.

9) Abiotic Resource Depletion Potential

As procedures 1, 3 and 4 do not use rare elements, their depletion of abiotic resources was negligible. These resource depletion indices (I_{ADP}) were, therefore, zero. Sulfur (S) in H_2SO_4 (route 3) has a low abiotic resource depletion potential, compared with antimony (Sb), the reference element.

$$ADP_i = \frac{(\text{depletion rate})_i / (\text{reserves})_i}{(\text{depletion rate})_{Sb} / (\text{reserves})_{Sb}} = 3.6 \cdot 10^{-4}$$

The abiotic depletion potential index I_{ADP} was calculated based on the mass of sulfur used, as sulfur constitutes 32.7% of the mass of H_2SO_4 . The abiotic resource depletion potential index for route 2 is expressed in equivalent grams of antimony.

$$I_{ADP} = \sum_i ADP_i \cdot m_i = ADP_S \cdot m_S = (3.6 \cdot 10^{-4}) \cdot (3.2 \cdot 10^{-2} g) = 1.09 \cdot 10^{-5} g$$

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