Electronic Supplementary Information for

Life cycle thinking case study for catalytic wet air oxidation of lignin in bamboo biomass for vanillin production

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Case Study

WAO processes enhance contact between molecular oxygen and the organic matter suspended or dissolved in water and then to eliminate organic compounds by oxidizing them, ideally to carbon dioxide and water, while also producing nitrogen and metal oxides. [1] However, in WAO processes, the oxidation is rarely complete and often leads to the production of materials like aldehydes and acids, which are also desirable, as the major products. This makes the exploration of WAO for conversion of lignin to value added products both a feasible and worthwhile pursuit, and such studies have already been reported using catalysts such as $CuSO_4$, MnO_2 and Fe_2O_3. [2]

In the current work $CuSO_4$ and Fe_2O_3 catalysts have been investigated for the WAO of bamboo lignin, and comparisons are reported for product yield/selectivity. The role of the base in WAO has been investigated by comparing the addition three different NaOH concentrations to the $CuSO_4$ catalyst system. NaOH was studied as it is widely used in lignin oxidation processes and for lignosulfonate oxidation. [3] Furthermore, the WAO of 'recycled lignin' which was produced as a by-product of the acid pyrolysis of cellulosic material in Miscanthus grass is also reported, herein. This allows an assessment of the potential of a circular economy as WAO of bamboo lignin and acid pyrolysis of cellulose will be complimentary in that the by-products of both processes can be used as feedstock for the other.

In general, metal oxide catalysts are common and it is known that mixed metal oxides provide additional desirable properties over single metal oxides. [4, 5] It has been suggested [6] that Cu^{2+} acts as an electron acceptor, accelerating the formation of the phenoxy radical, and that Fe^{3+} can form a new reactive intermediate, O_2-Fe^{3+}-lignin complex, which acts as an oxygen carrier and can attack lignin to form degradation products, thus enhancing the oxidation reaction.

Therefore the combination of $CuSO_4$ and Fe_2O_3 catalysts is worthy of further investigation and a number of different compositions of the mixed metal catalyst are also reported herein.

Lignin Determination: Klason Method[1]

The sample of approximately 1.0 g of bamboo powder (W1) was treated with 15 mL of 72% (v / v) sulfuric acid at room temperature for 2 h, followed by dilute sulfuric acid (3%) at reflux for 4 h. The solution was filtered, and the precipitate was used for determination of acid insoluble lignin gravimetrically. The ash content of the precipitate was dried at 105 °C then weighed (W2), and subtracted from the precipitate weight to give the measurement of acid insoluble lignin. The dry ash was burned in muffle furnace at 500°C for 1 h then cooled to room temperature and the ash content weighed (W3).

Acid-insoluble lignin was defined to be the residue, corrected for acid-insoluble ash, retained on a medium porosity filter crucible after the primary 72% and secondary 3% H_2SO_4 hydrolysis steps described in this procedure.

Klason experimental results were as followed:

W1=1.0065g

W2=0.2920g

W3=0.0021g

$$\%acid-insol.\,lignin = \frac{W2-W3}{W1} \times 100\% = \frac{0.2920-0.0021}{1.0065} = 28.80\%$$

where:

W1 = initial sample weight.

W2 = weight of crucible, acid-insoluble lignin, and acid-insoluble ash.

W3 = weight of crucible and acid-insoluble ash.

The sample used during the current work contained 28.8% of lignin.

Neutralisation of Formic Acid in recycled lignin

50 mL of the formic acid/lignin solution were placed in a 500 mL conical flask and cooled to 0 °C. In order to neutralise the formic acid, 8 M NaOH solution was slowly added until the

mixture was alkaline. The pH was measured, and more NaOH solution added until the pH reached 7. The total volume at this point was 100 mL.

Determining Lignin Content in formic acid lignin solution

After neutralisation of 50 mL of the formic acid/lignin solution (as above) the mixture was stirred vigorously by using a magnetic stirrer. After 10 minutes of stirring, the black liquid was transferred to centrifuge tubes then centrifuged for 15 minutes at 4000 rpm. The liquid was decanted from the solid lignin, the lignin washed with water on a Buchner funnel, and the solid dried at 105 °C for 48 hours. The weight of the lignin in 50 mL of the formic acid/lignin solution was recorded as 0.324g, i.e. 6.48 g L^{-1}.

HPLC Method

Table S1: HPLC Gradient Program

Time	%A	%B	%C	Flow ml/min
00:00	100	0	0	
10:00	75	25	0	
11:00	75	0	25	0.8
17:00	70	0	30	
17:30	70	30	0	
30:00	43	57	0	

A C18 ULTRASPHERE 5ODS column was used. The column temperature was maintained at 20 °C. For elution, a binary gradient program was used. Mobile phase A consisted of 8% acetic acid; phase B was composed of 8% acetic acid acid/methanol/acetonitrile (4:3:3 by volume). The pressure was regularly maintained between 75 and 125 bar. After each run, column and detector were flushed with solution A for 10 min.

HPLC sample preparation:

The samples were made into a 1 mg mL^{-1} solution with mobile phase. Separately introduced into identical containers were the unknown sample to be examined and each of the reference compounds avoiding contact between the sampling device and the samples.

Direct sample preparation: a 200 mg sample was taken directly from the oxidation reactor, to which was added 10 mL of mobile phase. The solution was filtered, then transferred to the HPLC vessel for analysis.

HPLC calibration standards:

25.0 mg of known standard was accurately weighed then transferred to a clean 25 mL volumetric flask and diluted to the mark with HPLC mobile phase. A series of dilutions of the stock 1.0 mg mL^{-1} solution was performed to obtain additional standards of 0.25 mg mL^{-1}, 0.50 mg mL^{-1}, 0.75 mg mL^{-1}. 10 mL of each of the standard were prepared using HPLC mobile phase. The solutions were sonicated for 10 min.

GC Method

The oven temperature was programmed to ramp from 65 to 140 °C at 6 °C min^{-1}, hold at 140 °C for 10 min, and then heated from 140 to 220 °C at 4 °C min^{-1} and held at 220 °C for 10 min.

GC calibration standards

30.0 mg of standards were weighed out accurately and then transferred to a clean 10 mL volumetric flask and diluted to the mark with chloroform. A series of dilutions of the stock 3 mg mL^{-1} solution was carried out to obtain additional standards of 0.75 mg mL^{-1}, 1.5 mg mL^{-1}, and 2.25 mg mL^{-1}. 10 mL of each of the dilutions was made up using chloroform. The solutions were sonicated for 10 min.

GC and HPLC calculation method:

$$AmountUnknown = \frac{Amount\ Standard}{Response\ Standard} * ResponseUnknown$$

	-	0.075 mol	0.15 mol	0.3 mol
■ 4-Hydroxyacetophenone	0.02%	0.26%	0.07%	0.45%
■ Acetovanillone	0.02%	0.35%	0.03%	0.34%
■ Acetosyringone	0.05%	0.73%	0.07%	0.54%
■ Vanillic acid	0.04%	0.02%	0.06%	0.14%
■ Syringic acid	0.07%	0.00%	0.00%	0.33%
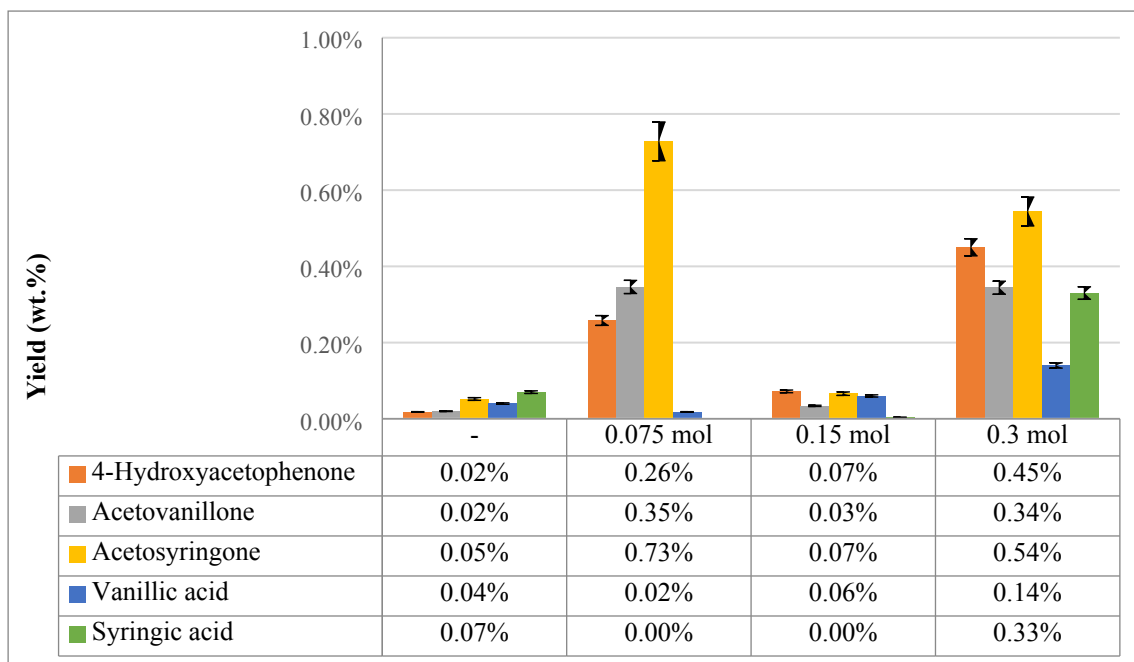
Figure S1: Yields of acids & ketones from NaOH promoted WAO of lignin over $CuSO_4$ catalyst; 4-Hydroxyacetophenone (orange), Acetovanillone (grey) and Acetosyringone (blue), Vanillic acid (yellow) and Syringic acid (green)

	CuSO4 (1.6)	CuSO4 (3.2)	Fe2O3 (0.8)	Fe2O3 (1.6)
4-Hydroxyacetophenone	0.28%	0.45%	0.23%	0.31%
Acetovanillone	0.22%	0.43%	0.37%	0.33%
Acetosyringone	0.36%	0.79%	0.82%	0.62%
Vanillic acid	0.28%	0.14%	0.10%	0.14%
Syringic acid	0.07%	0.28%	0.22%	0.06%

Figure S2: Yields of acids & ketones using different catalysts for WAO of lignin; 4-Hydroxyacetophenone (orange), Acetovanillone (grey) and Acetosyringone (blue), Vanillic acid (yellow) and Syringic acid (green)

	CuSO4 (0.8):Fe2O3 (0.8)	CuSO4 (1.6):Fe2O3 (1.6)	CuSO4 (1.1):Fe2O3 (2.1)	CuSO4 (2.1):Fe2O3 (1.1)
■ 4-Hydroxyacetophenone	0.28%	0.48%	0.34%	0.30%
■ Acetovanillone	0.28%	0.42%	0.30%	0.27%
■ Acetosyringone	0.46%	0.70%	0.55%	0.46%
■ Vanillic acid	0.07%	0.33%	0.09%	0.13%
■ Syringic acid	0.12%	0.08%	0.00%	0.00%

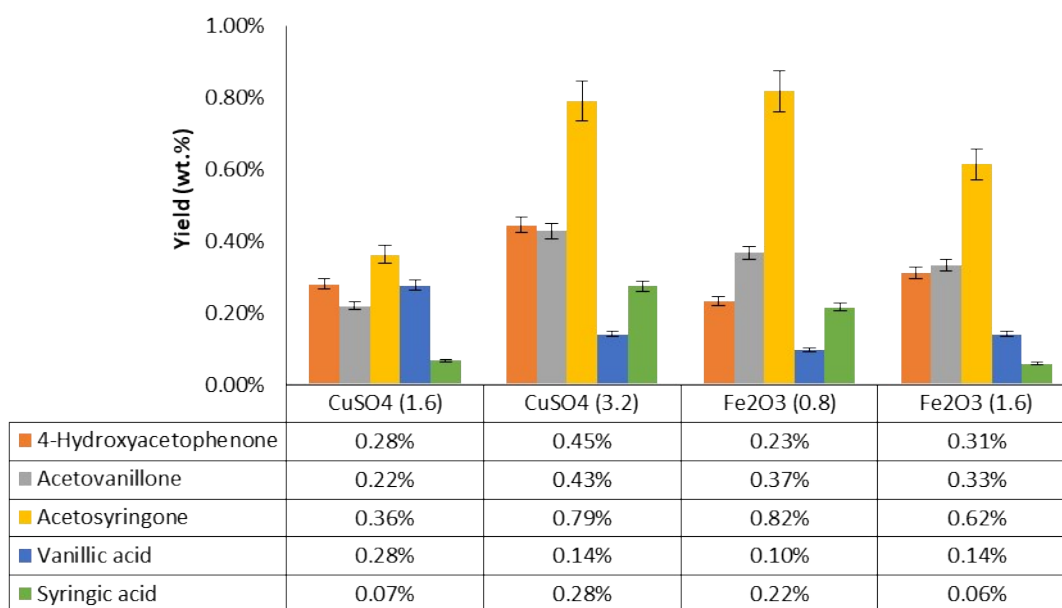**Figure S3:** Yields of acids & ketones using mixed catalysts for WAO of lignin; 4-Hydroxyacetophenone (orange), Acetovanillone (grey) and Acetosyringone (blue), Vanillic acid (yellow) and Syringic acid (green)

	Bamboo	Recycled Lignin
■ 4-Hydroxyacetophenone	1.89%	2.38%
■ Acetovanillone	0.42%	2.07%
■ Acetosyringone	0.48%	1.91%
■ Vanillic acid	0.33%	1.02%
■ Syringic acid	0.08%	

Figure S4: Yields of acids & ketones using mixed catalyst for WAO of bamboo and recycled lignin; 4-Hydroxyacetophenone (orange), Acetovanillone (grey) and Acetosyringone (blue), Vanillic acid (yellow) and Syringic acid (green)
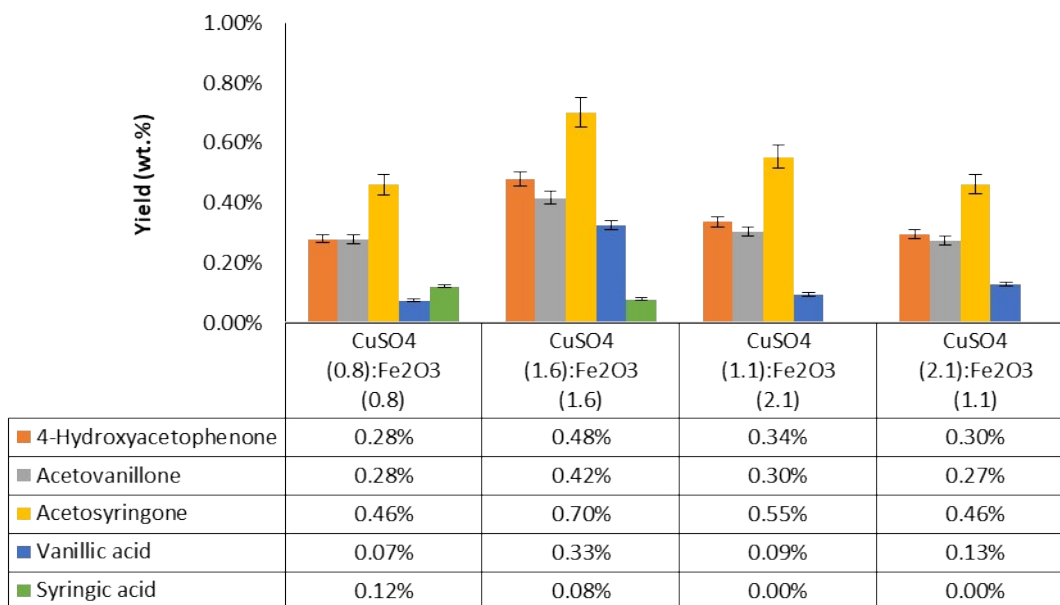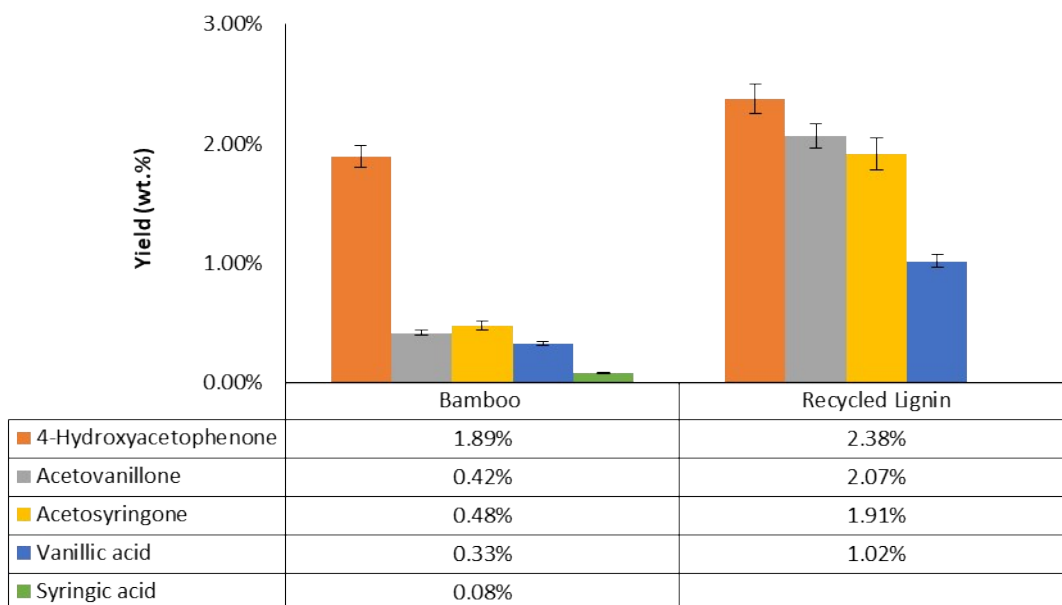
Table S2: Sulphuric Acid Synthesis

Compound Name	MW	AP/ g	OD P/g	SFP/ g	GWP /g	INHTP /g	INGTP/g	PER	ACCU Log Kow	ADP/g
Sulphur	32	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Oxygen	32	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Sulphur Dioxide	64	1	0	0.00	0.00	899.00	?	n/a	n/a	S= 6.77×10^{-5}
Water	18	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Sulphur Trioxide	80	1	0	0.00	0.00	?	?	n/a	n/a	S= 6.77×10^{-5}
Sulphuric Acid	98	1	0	0.00	0.00	0.000	187.00	n/a	n/a	S= 6.77×10^{-5}
Ammonium metavanadate	117	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Ammonia	17	0.93	0.00	0.00	0.00	58.12	3.13	n/a	n/a	0
Vanadium Oxide	182	0	0	0.00	0.00	?	?	n/a	n/a	V= 1.16×10^{-6}

Table S3: Wacker Process (Acetaldehyde Production)

Compound Name	MW	AP/g	ODP/g	SFP/g	GWP/g	INHTP/g	INGTP/g	PER	ACCU Log Kow	ADP/g
Ethylene	28	0	0	2.83	3.14	164	0.024	weeks	1.13	0
Oxygen	32	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Pd Ore	?	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Palladium	106	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Copper Oxide	80	0	0	0.00	0.00	?	?	n/a	n/a	0
Sodium Chloride	58	0	0	0.00	0.00	0.000	?	n/a	n/a	0
Chlorine	71	0	0	0.00	0.00	305	?	n/a	n/a	0
$PdCl_2$	177	0	0	0.00	0.00	0.000	?	n/a	n/a	Pd= 0.323 Cl =4.86×10^{-8}
Copper Chloride	134	0	0	0.00	0.00	0.000	?	n/a	n/a	Cu = 1.94E-03 Cl =4.86×10^{-8}
Acetaldehyde	44	0	0	2.05	2.00	2.880	155.000	weeks	-0.34	0
Chloroacetaldehyde	79	0	0	0.00	1.11	?	722.000	months	0.37	Cl =4.86×10^{-8}
Acetic Acid	60	0	0	0.16	1.47	0.007	55.000	weeks	-0.17	0
Chloromethane	51	0	0	0.01	0.86	16.90	0.49	months	0.91	Cl =4.86×10^{-8}

Table S4: Glyoxylic Acid Production

Compound Name	MW	AP/g	ODP/g	SFP/g	GWP/g	INHTP/g	INGTP/g	PER	ACCU Log Kow	ADP/g
Acetaldehyde	44	0	0	2.05	2.00	0.29	155.00	weeks	-0.34	0
Nitric Acid	63	0.7	0	0.00	0.00	0.04	1.33	n/a	n/a	0
Glyoxal	58	0	0	3.91	1.52	0.01	234.00	weeks	-0.85	0
Acetic Acid	60	0	0	0.21	1.47	0.02	55.00	weeks	-0.17	0
Formic Acid	46	0	0	0.02	1.91	0.09	536.00	weeks	-0.54	0
Glyoxylic Acid	74	0	0	0.00	1.19	0.00	0.00	weeks	-0.07	0
Oxalic Acid	90	0	0	0.00	0.98	0.00	1030.00	weeks	-0.81	0

Table S5: Haber Bosch & Nitric Acid Production

Compound Name	MW	AP/g	ODP/ g	SFP/ g	GWP/ g	INHTP/g	INGTP/ g	PER	ACCU Log Kow	ADP/g
Ammonia	17	0.93	0	0.00	0.00	58.12	3.13	n/a	n/a	0
Oxygen	32	0	0	0.00	0.00	0.00	0.00	n/a	n/a	0
Nitrogen Oxide (NO)	30	0.7	0	0.00	0.00	0.00	0.00	n/a	n/a	0
Water	18	0	0	0.00	0.00	0.00	0.00	n/a	n/a	0
Platinum	195	0	0	0.00	0.00	0.00	0.00	n/a	n/a	Pt= 1.29
Rhodium	103	0	0	0.00	0.00	0.00	0.00	n/a	n/a	Rh= 32.3
Nitrogen Dioxide (NO_2)	46	0.7	0	0.00	0.00	1725.80	0.00	n/a	n/a	0
Nitric Acid (HNO_3)	63	0.7	0	0.00	0.00	0.04	1.35	n/a	n/a	0
90 % Pt/10 % Rh	?	0	0	0.00	0.00	n/a	n/a	n/a	n/a	Pt= 1.29 Rh= 32.3
Methane	16	0	0	0.00	21.00	0.02	0.00	weeks	1.09	0
Carbon Monoxide	28	0	0	0.02	1.57	0.09	0.00	weeks	0.83	0
Hydrogen	2	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Carbon Dioxide	44	0	0	0.00	1.00	n/a	n/a	weeks	0.83	0
Nitrogen	28	0	0	0.00	0.00	0.00	0.00	n/a	n/a	0
Dinitrogen Tetraoxide (N_2O_4)	92	0.7	0	0.00	0.00	476.62	0.00	n/a	n/a	0
Nitrous Oxide (N_2O)	44	0.7	0	0.00	0.00	1744.10	0.00	n/a	n/a	0

Table S6: Nitrobenzene Production

Compound Name	MW	AP/ g	ODP/ g	SFP/ g	GWP/ g	INHTP/ g	INGTP/g	PER	ACCU Log Kow	ADP/g
Benzene	78	0	0	0.22	3.38	1.33	0.62	weeks	2.13	0
Nitric Acid	63	0.7	0	0.00	0.00	0.04	1.35	n/a	n/a	0
Sulphuric Acid	98	1	0	0.00	0.00	0.00	187.00	n/a	n/a	S= 6.77x10^{-5}
Nitrobenzene	123	0	0	0.02	2.15	2.07	34.90	months	1.85	0
Water	18	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0

Table S7: Hydrogen Peroxide Production

Compound Name	MW	AP/ g	ODP/ g	SFP/ g	GWP/ g	INHTP/ g	INGTP/g	PER	ACCU Log Kow	ADP/g
Toluene	92	0	0	0.00	3.35	1.00	1.00	months	2.56	0
Benzene	78	0	0	0.22	3.38	1.33	0.62	weeks	2.13	0
Ethylbenzene	106	0	0	2.06	3.32	2.45	0.12	months	3.15	0
m-xylene	106	0	0	3.07	3.32	1.86	0.08	months	3.2	0
p-xylene	106	0	0	1.84	3.32	2.16	0.11	months	3.15	0
o-xylene	106	0	0	2.40	3.32	1.57	0.12	months	3.12	0
Phthalic anhydride	148	0	0	0.81	2.38	?	16.70	months	1.6	0
Aluminium Chloride	133	0	0	0.00	0.00	?	?	n/a	n/a	0
2-Ethylanthraquinone	236	0	0	0.00	0.00	?	2.84	months	4.37	0
Hydrogen	2	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Oxygen	32	0	0	0.00	0.00	n/a	n/a	n/a	n/a	0
Hydrogen Peroxide	34	0	0	0.00	0.00	0.05	3140.00	n/a	n/a	0
Naphthalene	128	0	0	1.05	3.44	62.30	11.40	months	3.3	0

Table S8: Chloroform Production

Compound Name	MW	AP/g	ODP/g	SFP/g	GWP/g	INHTP/g	INGTP/g	PER	ACCU Log Kow	ADP/g
Methane	16	0	0	4.52×10^{-3}	21	0.02	0.00	weeks	1.09	0
Chlorine	71	0	0	0	0	308.81	0.00	n/a	n/a	Cl $=4.86 \times 10^{-8}$
Chloromethane	50	0	0.02	1.16×10^{-2}	12	17.22	0.50	months	0.91	Cl $=4.86 \times 10^{-8}$
Dichloromethane	85	0	0	1.26×10^{-2}	9	0.99	1.58	months	1.25	2 Cl $=9.72 \times 10^{-8}$
Chloroform	119	0	0	6.45×10^{-3}	16	0.78	1.33	months	1.97	3 Cl $=1.458 \times 10^{-7}$
Tetrachloromethane	158	0	1.1	0	1730	3.62	0.04	months	2.83	4 Cl $=5.832 \times 10^{-7}$
Hydrogen Chloride	36	0	0	0	0	0.16	1.74	n/a	n/a	Cl $= 4.86 \times 10^{-8}$

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