Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Guidelines to Design Electrolytes for Lithium-ion Batteries: Environmental impact, Physicochemical and Electrochemical Properties

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Acronyms

Acronyms	Usual name	IUPAC name
1,3-DL	Dioxolane	1,3-dioxolane
2FEA	Fluoroethyl acetate	2-fluoroethyl acetate
2FEP	Fluoroethyl propionate	2-fluoroethyl propionate
2FPMC	2-fluoropropyl methyl carbonate	2-fluoropropyl methyl carbonate
2Me-1,3-DL	2-methyl dioxolane	2-methyl-1,3-dioxolane
2Me-THF	Methyltetrahydrofuran	2-methyltetrahydrofuran
3Me-SL	3-methylsulfolane	3-methyltetrahydrothiophene 1,1-dioxide
4Me-1,3-DL	4-methyl dioxolane	4-methyl-1,3-dioxolane
A	Average	
ALOP	Agricultural land occupation potential	
APOS	Allocation at the point of substitution	
BC	1,2-butylene carbonate	4-ethyl-1,3-dioxolan-2-one
CH_3Cl	Methyl chloride	Chloromethane
ClMB	Chloromethyl butyrate	Chloromethyl butyrate
cP	Centipoise (mPa.s)	
DEC	Diethyl carbonate	Diethyl carbonate
DEE	Diethoxyethane	1,2-diethoxyethane
DES	Diethyl sulfite	Diethyl sulfite
DFEMC	Difluoroethyl methyl carbonate	2,2-difluoroethyl methyl carbonate
DFEME	Difluoroethoxy methoxy ethane	1,1-difluoro-2-(2-methoxyethoxy)ethane
DMC	Dimethyl carbonate	Dimethyl carbonate
DME	Dimethoxyethane	1,2-dimethoxyethane
DMM	Dimethoxymethane	Dimethoxymethane
DMS	Dimethyl sulfite	Dimethyl sulfite
DMSO	Dimethyl sulfoxide	(methylsulfinyl)methane
DPS	Dipropyl sulfone	1-(propylsulfonyl)propane
DSC	Differential scanning calorimetry	
DVL	δ-valerolactone	Tetrahydro-2H-pyran-2-one
EA	Ethyl acetate	Ethyl acetate
EB	Ethyl butyrate	Ethyl butyrate
EC	Ethylene carbonate	1,3-dioxolan-2-one
ED	Damage to ecosystems diversity	
EDFA	Ethyl difluoroacetate	Ethyl 2,2-difluoroacetate
EDFEC	Ethyl difluoroethyl carbonate	2,2-difluoroethyl ethyl carbonate
EDFEE	Ethoxy difluoroethoxy ethane	2-(2-ethoxyethoxy)-1,1-difluoroethane
EFA	Ethyl fluoroacetate	Ethyl 2-fluoroacetate
EFEC	Ethyl fluoroethyl carbonate	Ethyl (2-fluoroethyl) carbonate
EFEE	Ethoxy fluoroethoxy ethane	1-ethoxy-2-(2-fluoroethoxy)ethane
EG	Ethylene glycol	ethane-1,2-diol)

EGME	Ethylene gycol monomethyl ether	2-Methoxyethanol
EiBS	Ethyl isobutyl sulfone	1-(ethylsulfonyl)-2-methylpropane
EiPC	Ethyl isopropyl carbonate	Ethyl isopropyl carbonate
EiPS	Ethyl isopropyl sulfone	2-(ethylsulfonyl)propane
EMC	Ethyl methyl carbonate	Ethyl methyl carbonate
EME	Ethoxy methoxy ethane	1-ethoxy-2-methoxyethane
EMEES	Ethyl methoxyethoxyethyl sulfone	1-(ethylsulfonyl)-2-(2-methoxyethoxy)ethane
EMES	Ethyl methoxyethyl sulfone	1-methoxy-2-(ethylsulfonyl)ethane
EMS	Ethyl methyl sulfone	(methylsulfonyl)ethane
EO	Ethylene oxide	Oxirane
Eox	Oxidation Potential	
EPC	Ethyl propyl carbonate	Ethyl propyl carbonate
EPE	Ethyl propyl ether	1-ethoxypropane
ES	Ethylene sulfite	1,3,2-dioxathiolane 2-oxide
EsBS	Ethyl secbutyl sulfone	2-(ethylsulfonyl)butane
ESCP	Ethyl cyclopentyl sulfone	(ethylsulfonyl)cyclopentane
EtBr	Ethyl bromide	Bromoethane
ETFEC	Ethyl trifluoroethyl carbonate	Ethyl (2,2,2-trifluoroethyl) carbonate
ETFEE	Ethoxy trifluoroethoxy ethane	2-(2-ethoxyethoxy)-1,1,1-trifluoroethane
EtSH	Ethyl mercaptan	Ethanethiol
EVS	Ethyl vinyl sulfone	(ethylsulfonyl)ethene
FDP	Fossil depletion potential	
FEC	Fluoroethylene carbonate	4-fluoro-1,3-dioxolan-2-one
FEME	Fluoroethoxy methoxy ethane	1-fluoro-2-(2-methoxyethoxy)ethane
FEP	Freshwater eutrophication potential	
FETP	Freshwater ecotoxicity potential	
FGBL	Fluoro-γ-butyrolactone	3-fluorodihydrofuran-2(3H)-one
FMS	Fluoro methyl sulfone	Methanesulfonyl fluoride
FPC	Fluoropropylene carbonate	4-(fluoromethyl)-1,3-dioxolan-2-one
FPMC	Fluoropropyl methyl carbonate	3-fluoropropyl methyl carbonate
FPMS	Trifluoropropyl methyl sulfone	1,1,1-trifluoro-3-(methylsulfonyl)propane
FS	Fluorophenyl methyl sulfone	1-fluoro-2-(methylsulfonyl)benzene
GBL	γ-butyrolactone	dihydrofuran-2(3H)-one
GC	Glassy Carbon	
GWP	Global warming potential	
H	Hierarchist	
HH	Damage to human health	
HTP	Humantoxicity potential	
iPMS	Isopropyl methyl sulfone	2-(methylsulfonyl)propane
LiBs	Lithium-Ion Batteries	
LCA	Life Cycle Assessment	
LCI	Life Cycle Inventory	
LCIA	Life Cycle Impact Assessment	
$LiAsF_6$	Lithium hexafluoroarsenate(V)	Lithium hexafluoroarsenate(V)
$LiBF_4$	Lithium tetrafluoroborate	Lithium tetrafluoroborate

LiCl	Lithium chloride	Lithium chloride
$LiC(SO_2CF_3)_3$	Li Methide	Lithium tris(trifluoromethanesulfonyl)methide
LFP	Lithium iron phosphate	
LMO	Lithium ion manganese oxide	
$LiPF_6$	Lithium hexafluorophosphate	Lithium hexafluorophosphate
LPG	Liquefied Petroleum Gas	
LiTf	Lithium triflate	Lithium trifluoromethanesulfonate
LiTFSI	Lithium bis((trifluoromethyl)sulfonyl)amide	Lithium bis((trifluoromethyl)sulfonyl)amide
MA	Methyl Acetate	Methyl acetate
MAN	Maleic Anhydride	Furan-2,5-dione
MB	Methyl butyrate	
MCA	Methyl cyanoacetate	Methyl 2-cyanoacetate
MDP	Mineral depletion potential	
MEMS	Methoxyethyl methyl sulfone	1-methoxy-2-(methylsulfonyl)ethane
MEP	Marine eutrophication potential	
MeSH	Methyl mercaptan	Methanethiol
METP	Marine ecotoxicity potential	
MFDMC	Monofluorodimethyl carbonate	Fluoromethyl methyl carbonate
MFEMC	Monofluoroethyl methyl carbonate	2-fluoroethyl methyl carbonate
MiPC	Methyl isopropyl carbonate	Isopropyl methyl carbonate
MMOA	Methyl methoxy acetate	Methyl 2-methoxyacetate
MPA	Methoxypropyl acetate	1-methoxypropan-2-yl acetate
MPC	Methyl propyl carbonate	Methyl propyl carbonate
MTS	Methyl trimethylene sulfone	2-methylthietane 1,1-dioxide
MS	Dimethyl sulfone	(methylsulfonyl)methane
NLTP	Natural land transformation potential	
NCA	Nickel-Cobalt-Aluminum	
NMC	Lithium Nickel Manganese Cobalt Oxide	
ODP	Ozone depletion potential	
PC	Propylene carbonate	4-methyl-1,3-dioxolan-2-one
PFPMC	Pentafluoropropyl methyl carbonate	Methyl (2,2,3,3,3-pentafluoropropyl) carbonate
PMFP	Particle matter formation potential	
POFP	Photochemical oxidant formation potential	
PS	Propylene sulfite	4-methyl-1,3,2-dioxathiolane 2-oxide
RA	Damage to resource availability	
SL	Sulfolane	Tetrahydrothiophene 1,1-dioxide
TAP	Terrestrial acidification potential	
TeFPMC	Tetrafluoropropyl methyl carbonate	Methyl (2,2,3,3-tetrafluoropropyl) carbonate
TETP	Terrestrial ecotoxicity potential	
TFEMC	Trifluoroethyl methyl carbonate	Methyl (2,2,2-trifluoroethyl) carbonate
TFEME	Trifluoroethoxy methoxy ethane	1,1,1-trifluoro-2-(2-methoxyethoxy)ethane
THF	Tetrahydrofuran	Tetrahydrofuran
TMS	Tetramethylene sulfone	Tetrahydrothiophene 1,1-dioxide
TrFPMC	Trifluoropropyl methyl carbonate	Methyl (3,3,3-trifluoropropyl) carbonate

ULOP	Urban land occupation potential	
V	Volt	
VC	Vinylcarbonate	1,3-dioxol-2-one
VEC	Vinyl ethylene carbonate	4-vinyl-1,3-dioxolan-2-one

Contents

1. Synthesis of MPA, MEMS and EMEES

1.1. Procedures

1.1.1. MPA (**2**) [1]

1-methoxy-2-propanol **1** (10 mL, 0.102 mol) was introduced in a three-neck flask equipped with a condenser, a thermometer and an addition funnel. The system was placed under argon atmosphere, and acetic anhydride (52.2 mL, 0.55 mol) was added dropwise at a temperature of 50 °C. After the addition was complete, the solution was heated to 150 °C for 16 h (TLC using cyclohexane/ethyl acetate as eluent indicated a completion of the reaction). The solution was cooled to 0 °C and neutralized with a saturated solution of $NaHCO_3$. The mixture was extracted with Et_2O (3x), and the combined organic layers were dried over Na_2SO_4, filtered, and the solvent evaporated under reduced pressure to provide a crude product which was purified by distillation (Eb= 144-147 °C at atmospheric pressure) to furnish 10.15 g of **2** (75%) as a colorless liquid.

R_f (cyclohexane/ethyl acetate; 6/4): 0.68

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.12 – 5.00 (m, 1H), 3.49 – 3.37 (m, 2H), 3.36 (s, 3H), 2.05 (s, 3H), 1.22 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.14, 75.61, 69.83, 59.68, 21.83, 17.11.

GC-MS RT: 7.04min, *m/z* 133.06 [MH^+], 150.07 [MNH_4^+]

1.1.2. MEMS (**5**) [2],[4]

To 4.6 g of NaH (0.115 mol), 60 % dispersion in oil and previously washed with pentane) in dry THF (50 mL) and cooled to 0 °C, was added dropwise β-mercaptoethanol **3** (2.7 mL, 0.0384 mol) diluted in THF (10 mL). The mixture was stirred for 30 min at this temperature, and iodomethane (6.22 mL, 0.1 mol) was then added carefully. The solution was stirred for an additional 1 h (TLC indicated the completion of the reaction). The mixture was hydrolyzed with water and extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and the solvent evaporated under vacuum to afford 4.69 g of crude yellow liquid **4** which was used without purification.

To a three-neck flask equipped with a thermometer, a condenser, and an addition funnel containing a solution of 35 % w/w H_2O_2 (6.6 mL, 0.077 mol) cooled to 0 °C (ice bath), was added under argon crude **4** (4.69 g) in a way to maintain the temperature below 30 °C. The ice bath was removed and the solution was heated at 75 °C for 16 h. The reaction mixture was concentrated by evaporation under vacuum to provide crude **5** (5.1 g) which was purified by column chromatography (cyclohexane/ethyl acetate; from 7/3 to 5/5) to provide pure **5** (2.6 g, 49 %) as a colorless oil.

R_f (cyclohexane/ethyl acetate; 6/4): 0.25

^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.82 – 3.74 (m, 1H), 3.36 (d, *J* = 0.7 Hz, 1H), 3.22 – 3.16 (m, 1H), 2.95 (dd, *J* = 1.4, 0.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 66.51, 59.29, 55.44, 43.32.

GC-MS RT: 8.77min, *m/z* 156.07 [MNH_4^+]

1.1.3. EMEES (**9**) [3],[4]

To a two-neck flask equipped with a condenser and an addition funnel, was introduced a $CHCl_3$ solution (10 mL) of diglyme monomethyl ether **6** (3.91 mL, 0.033 mol) and pyridine (2.69 mL, 0.033 mol). The system was placed under argon, and a solution of $SOCl_2$ (3.12 mL, 0.042 mol) in $CHCl_3$ (10 mL) was added slowly at r.t.. The reaction was heated at 65°C for 3.5 h when TLC (cyclohexane/ethyl acetate; 6/4) indicated the end of the reaction. The reaction mixture was cooled with an ice bath and quenched slowly with water. The organic layer was washed with water, dried over Na_2SO_4 filtered and concentrated by evaporation under reduced pressure to provide 6.37 g of crude pale yellow liquid **7**, which was used without purification in the next step (^1H NMR spectra revealed only traces of impurities).

In a two-neck round-bottom flask containing 15 mL of dry methanol, was added sodium (644 mg, 0.028 mol) and the system was flushed with argon. After complete consumption of sodium, ethanethiol (2.07 mL, 0.028mol) was introduced and the solution was stirred for 2h at room temperature. Crude **7** (3.9 g, 0.028mol) dissolved in 10 mL of dry methanol was added to the reaction mixture. The flask was equipped with a condenser, and the solution was heated at 75°C for 2h and checked by TLC (cyclohexane/ethyl acetate; 8/2). At the end of the reaction, the mixture was evaporated, filtered, rinsed with EtOAc, and the filtrate was concentrated under reduced pressure to afford 4.33g of crude **8** which was pure enough to be used without purification in the next step.

Crude **8** (4.3 g, 0.025 mol) was introduced in a three-neck round-bottom flask equipped with a condenser, a thermometer and an addition funnel containing concentrated H_2O_2 (35% w/w, 4.3 mL, 0.05 mol). The system was flushed with argon and cooled to 0°C with an ice bath. Then a very slow addition of concentrated H_2O_2 was performed to maintain the temperature below 30°C. The ice bath was then removed and the reaction was heated at 75°C overnight. After 16h the reaction was checked by TLC (cyclohexane/ethyl acetate; 5/5), the reaction mixture was concentrated by evaporation under reduced pressure to afford 4.3 g of crude **9**. The product was purified by column chromatography (cyclohexane/ethyl acetate; from 5/5 to pure EtOAc) to afford 2.44 g (58%) of **9** as a colorless oil.

R_f (cyclohexane/ethyl acetate; 5/5): 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ : 3.92 – 3.82 (m, 1H), 3.62 – 3.56 (m, 1H), 3.52 – 3.45 (m, 1H), 3.32 (dd, *J* = 1.9, 1.3 Hz, 1H), 3.16 (t, *J* = 5.2 Hz, 1H), 3.09 (q, *J* = 7.5 Hz, 1H), 1.34 (ddd, *J* = 7.4, 1.9, 1.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 72.01, 70.99, 65.23, 59.38, 53.06, 49.60, 6.88.

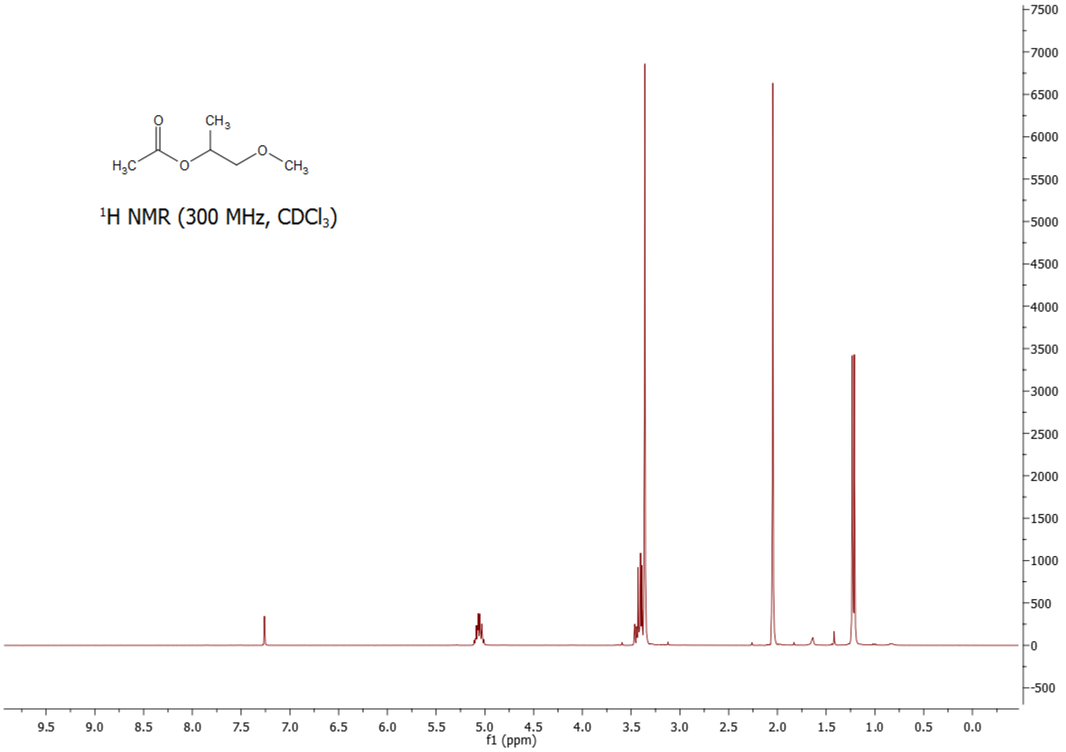
GC-MS RT: 13.82min, m/z 214.14 [MNH_4^+]

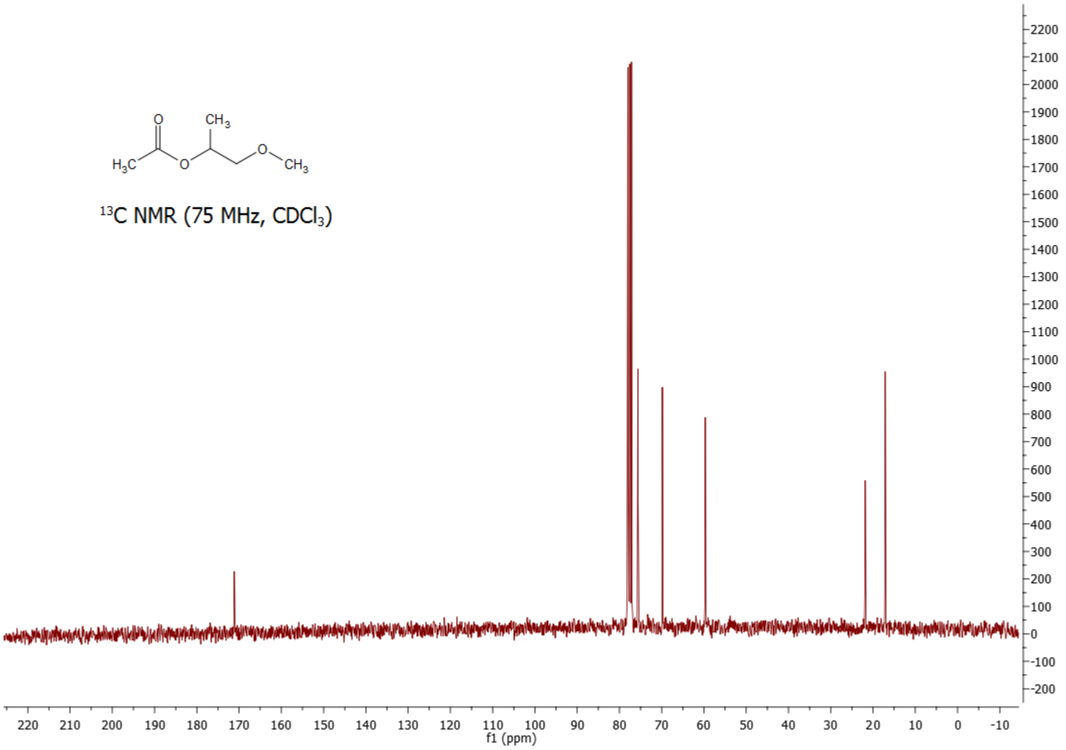
References:

[1] W. J. Bailey, L. Nicholas, *J. Org.Chem.*, 1956, **21**, 648.
[2] T. Takeda, H. Furukawa, M. Fujimori, K. Suzuki, T. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1863.
[3] X.-G. Sun, C. A. Angell, *Electrochem. Commun.*, 2005, **7**, 261.
[4] M. Jereb, *Green Chem*., 2012, **14**, 3047.

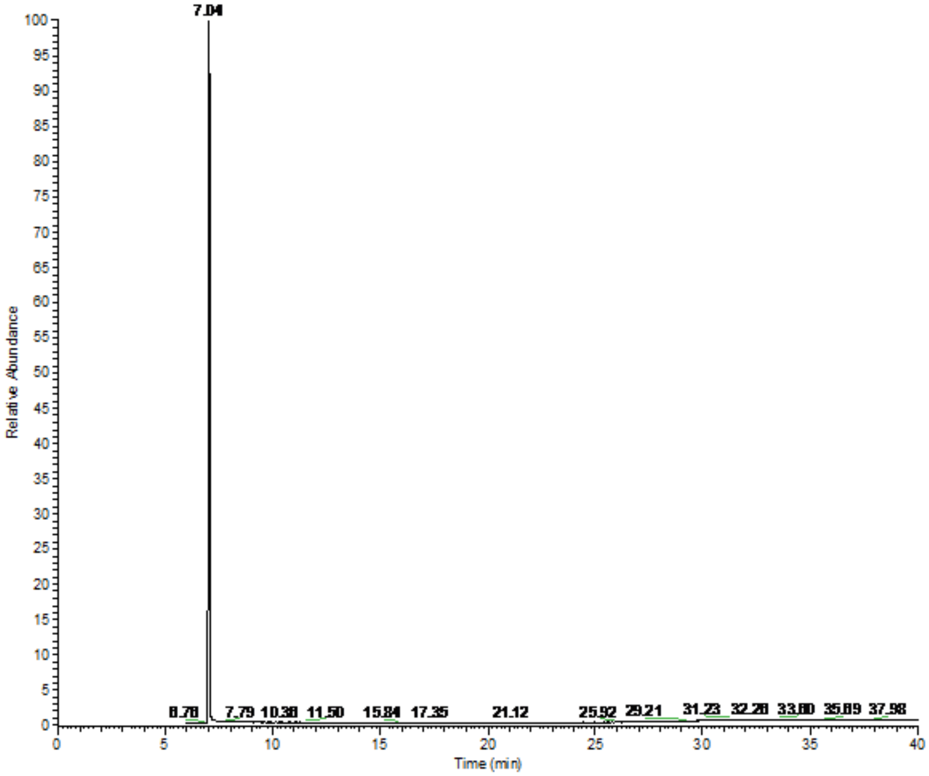
1.2. Spectra

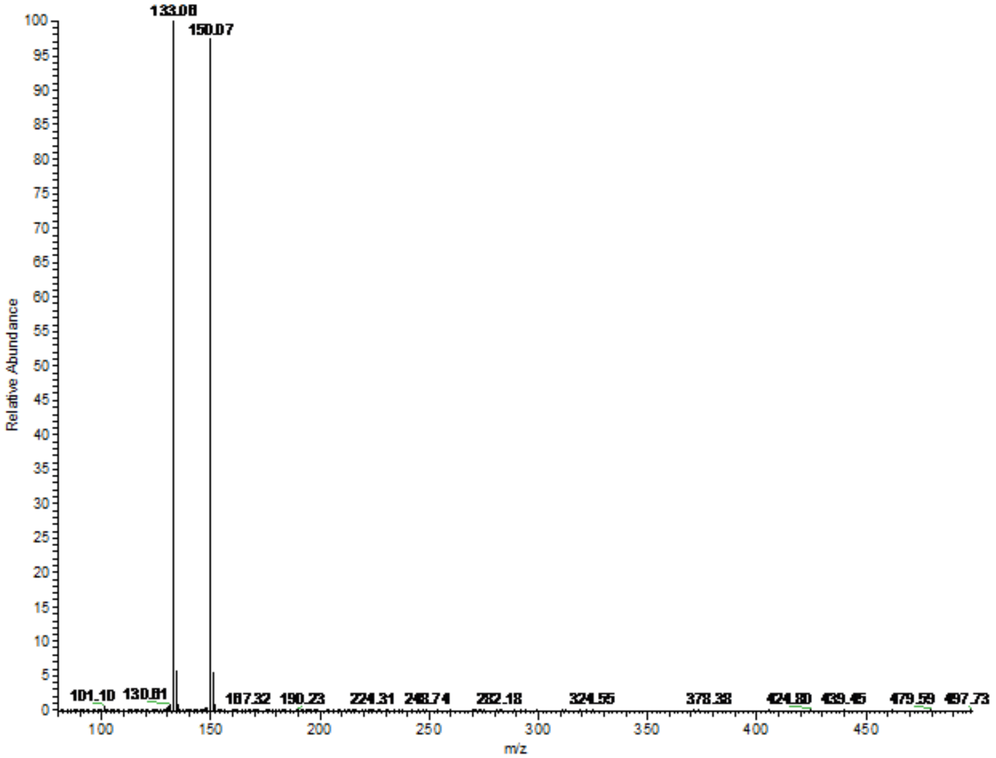
1.2.1. MPA (**2**)



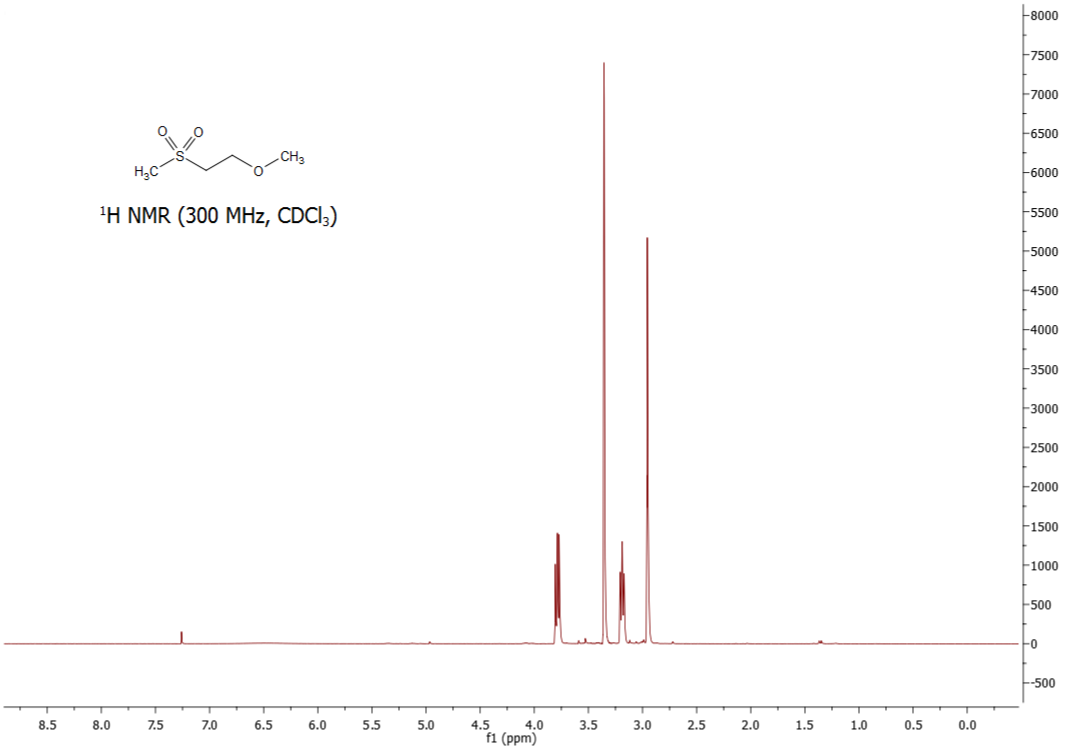


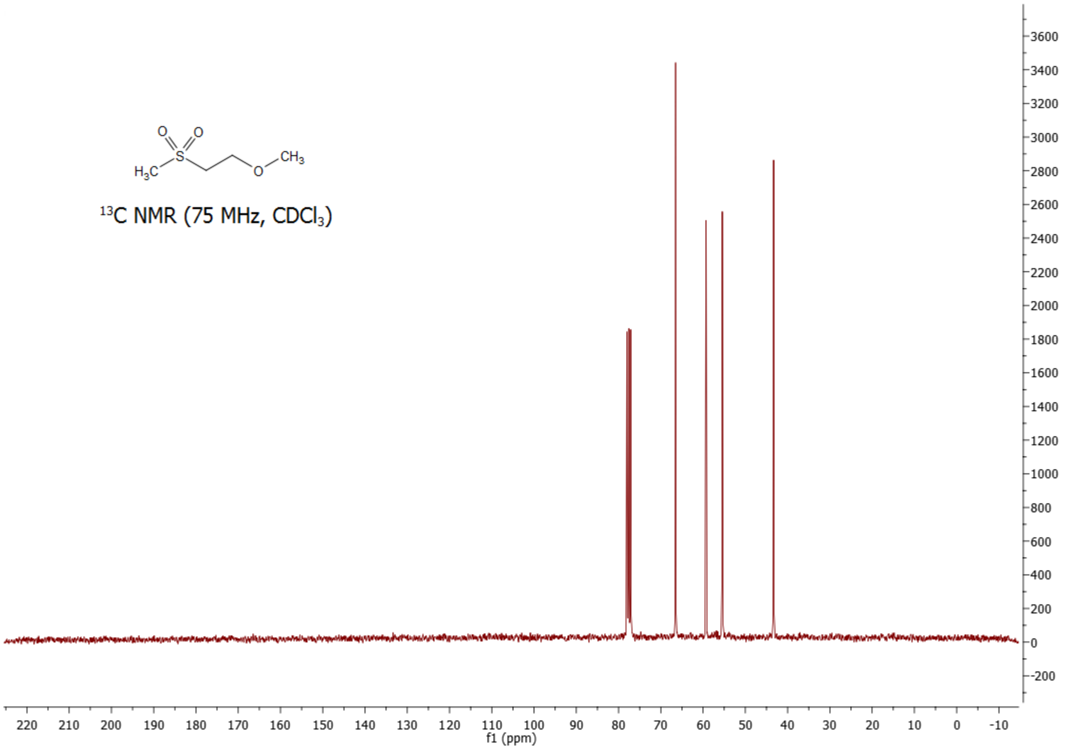
GC-MS (CI)


7.04
6.78
7.79
10.38
11.50
15.84
17.35
21.12
25.92
29.21
31.23
32.28
33.80
35.89
37.98
Relative Abundance
Time (min)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

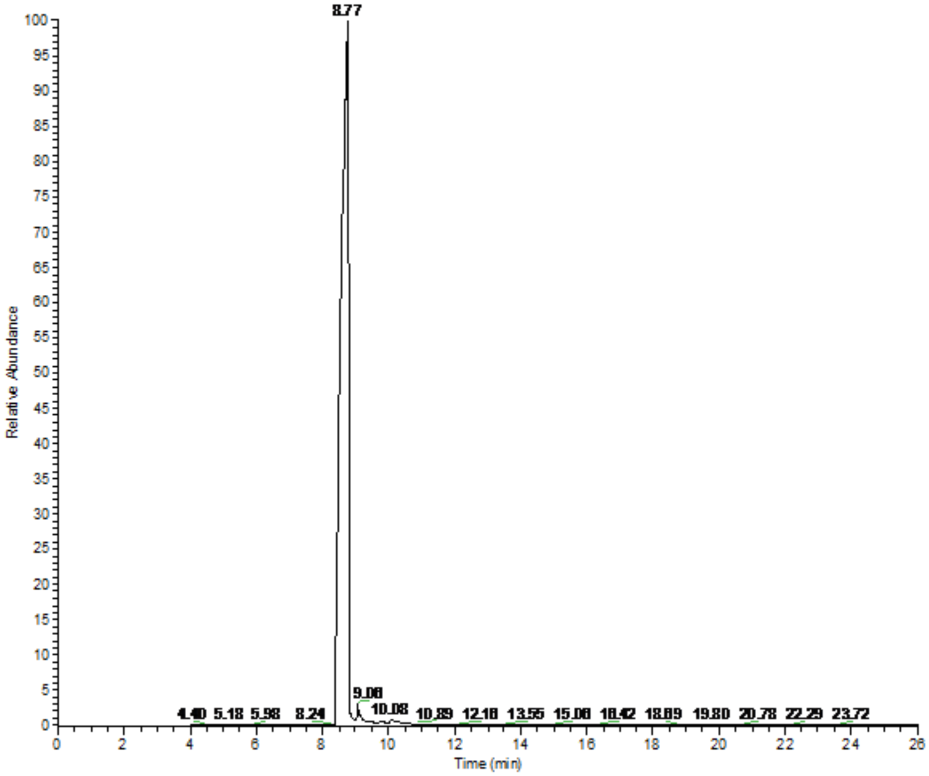

133.08
150.07
101.10
130.81
167.32
190.23
224.31
248.74
282.18
324.55
378.38
424.80
439.45
479.59
497.73
Relative Abundance
m/z
100
150
200
250
300
350
400
450

1.2.2. MEMS (**5**)


O
O
S
H$_3$C
O
CH$_3$
^{1}H NMR (300 MHz, CDCl$_3$)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
S
H$_3$C
O
CH$_3$
^{13}C NMR (75 MHz, CDCl$_3$)
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

GC-MS (CI)



8.77
9.06
10.08
4.40
5.18
5.98
8.24
10.89
12.18
13.55
15.06
16.42
18.09
19.80
20.78
22.29
23.72
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
0
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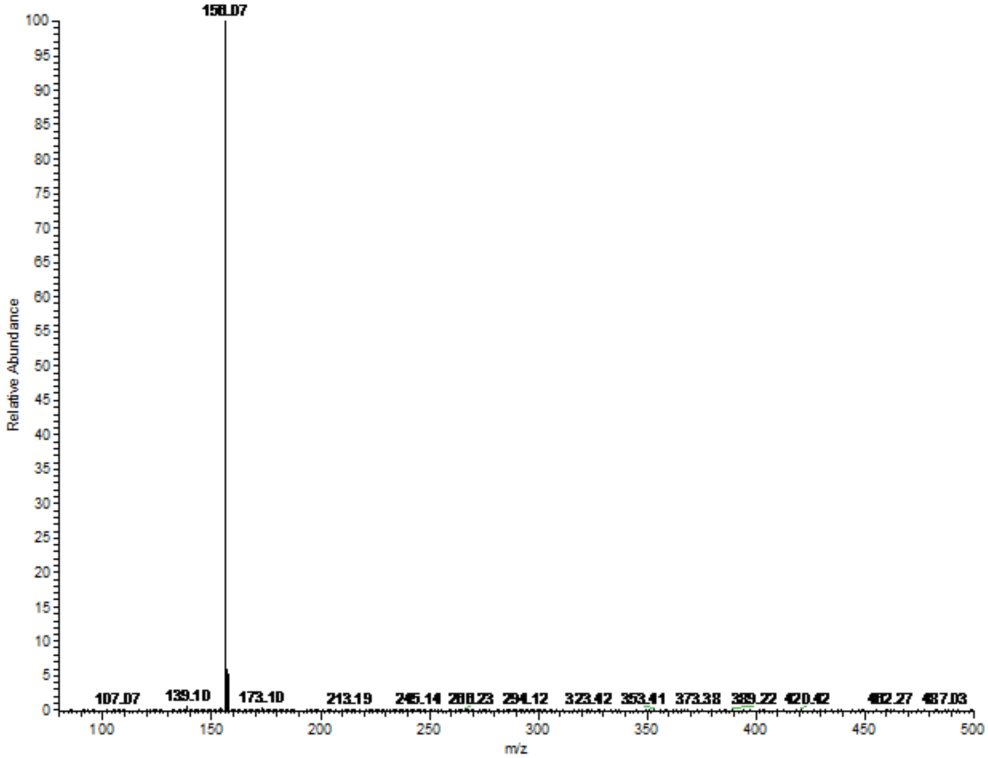
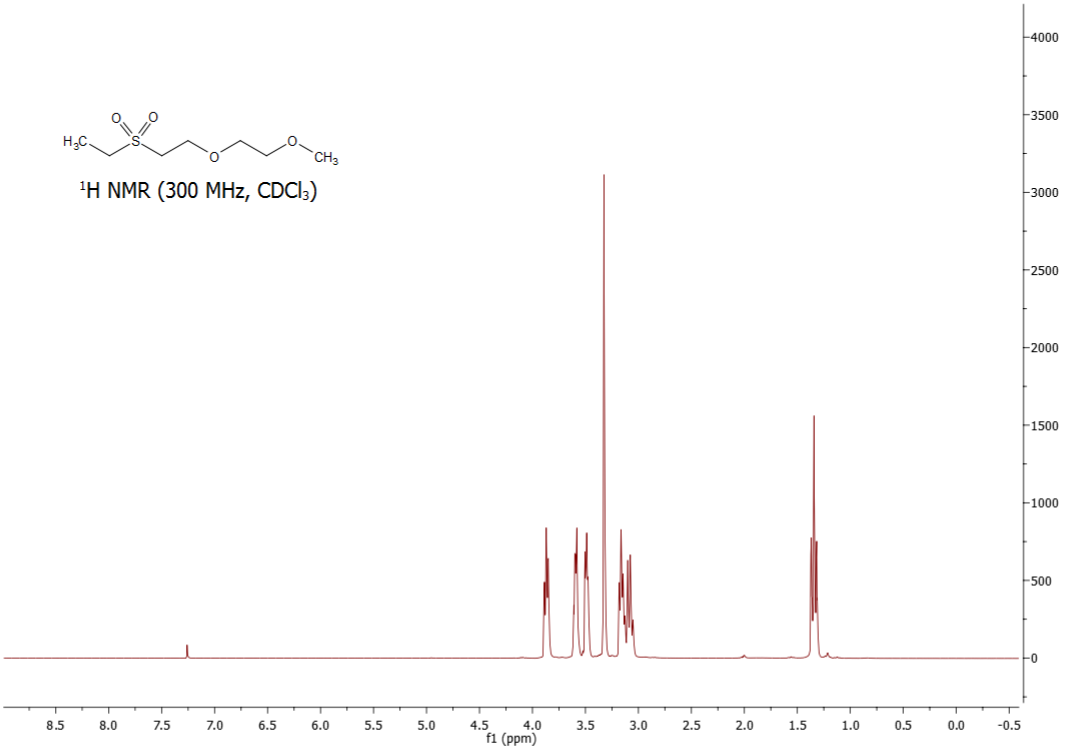
16
18
20
22
24
26
Time (min)

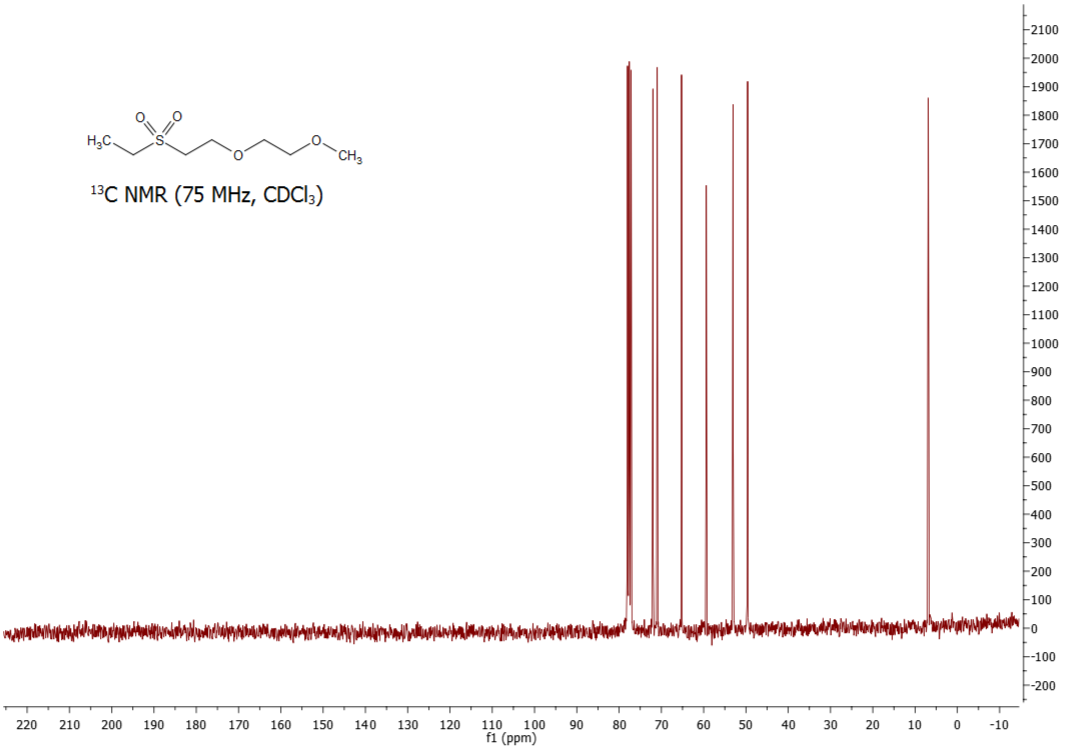


156.07
107.07
139.10
173.10
213.19
245.14
268.23
294.12
323.42
353.41
373.38
389.22
420.42
462.27
487.03
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
100
150
200
250
300
350
400
450
500
m/z

1.2.3. EMEES (**9**)

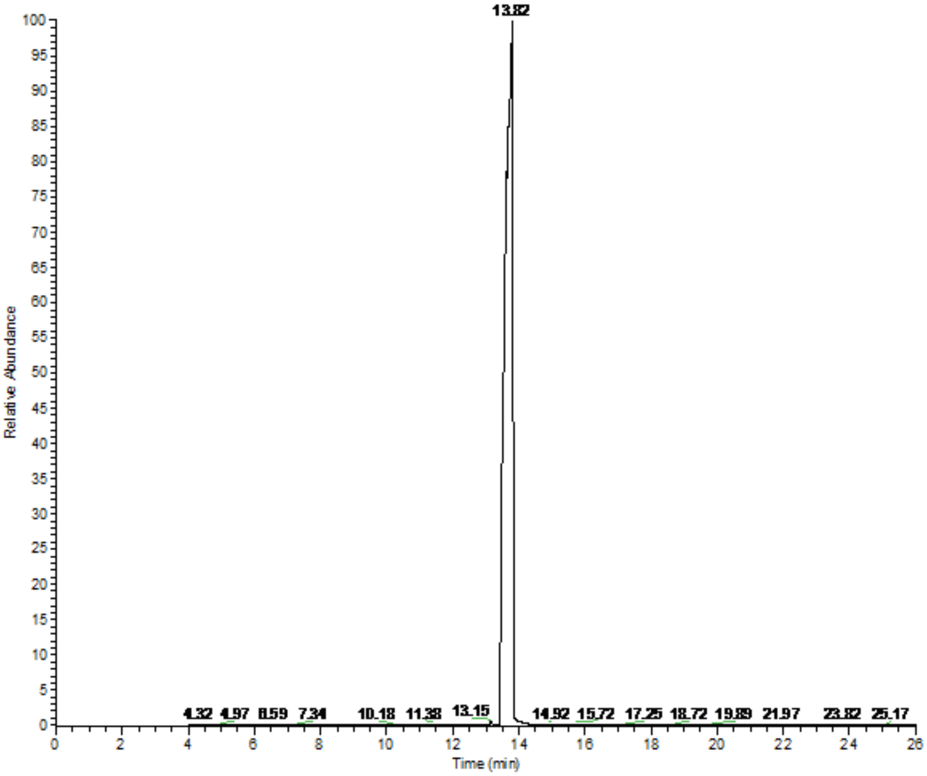


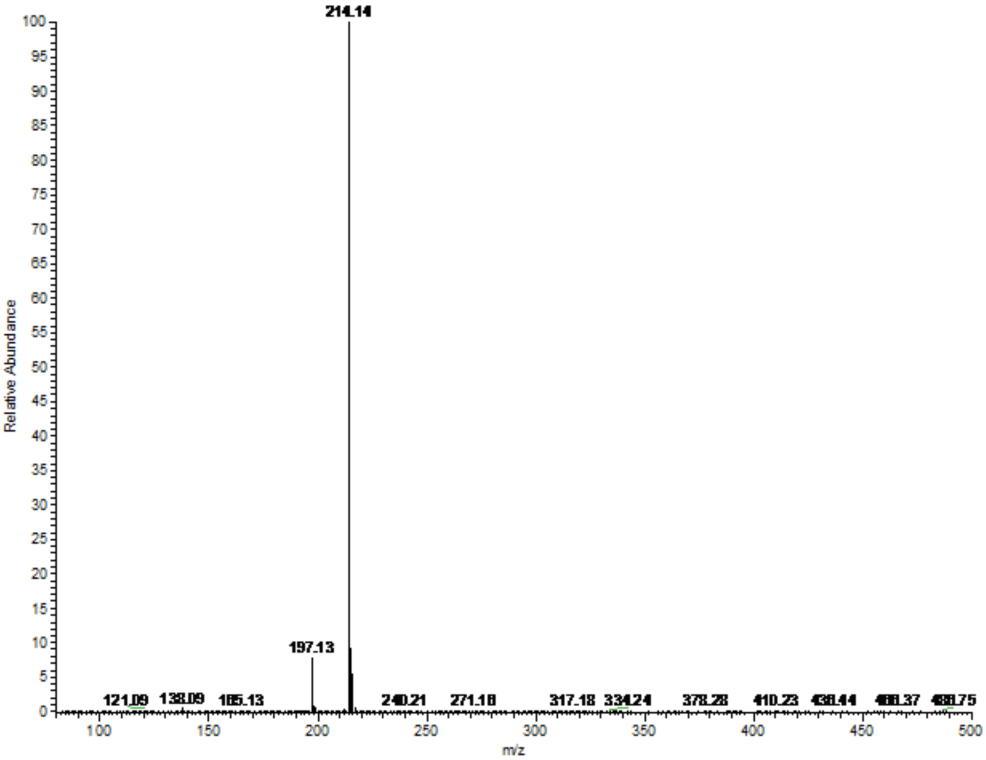
H_3C S O O O O CH_3
^{1}H NMR (300 MHz, $CDCl_3$)
4000
3500
3000
2500
2000
1500
1000
500
0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



H_3C S O O O O CH_3
^{13}C NMR (75 MHz, $CDCl_3$)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

GC-MS (CI)


13.82
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4.32
4.97
6.59
7.34
10.18
11.38
13.15
14.92
15.72
17.25
18.72
19.89
21.97
23.82
25.17
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Time (min)


214.14
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
197.13
121.09
138.09
165.13
240.21
271.18
317.18
334.24
378.28
410.23
438.44
466.37
488.75
100
150
200
250
300
350
400
450
500
m/z

2. Introduction to LCA

The objective of this work is to develop Life Cycle Inventories (LCI) for a number of solvents used in lithium-ion batteries as electrolytes. For most solvents, several production routes have been evaluated. The LCI of some of these electrolytes are already included in Ecoinvent (Table 1) or in LCA literature. [1,2]

Table 1Solvents and their production routes.

		Route	LCI in Ecoinvent 3.2.	LCI in literature	Original LCI
Carbonates	Dimethyl carbonate (DMC)	Shell Omega process		✓	✓
	Ethylene carbonate (EC)	From ethylene oxide and CO_2	✓		
Esters	Ethyl acetate (EA)	Fischer esterification	✓		
		Dehydrogenation pathway			✓
		Avada process			✓
		Butane oxidation	✓		
	γ-butyrolactone (GBL)	Reppe process	✓		
		Maleic anhydride pathway			✓
Ethers	Dimethoxyethane (DME)	Cleavage of ethylene oxide in presence of dimethyl ether	✓		
		DOW process			✓
		Shell Omega process			✓
		Hydration/coupling pathway			✓
	Tetrahydrofuran (THF)	Reppe process	✓		
		Hydrogenation of maleic anhydride			✓
		Mitsubishi acetoxylation			✓
Sulfones	Sulfolane (SL)	Hydrogenation of sulfolene			✓
	Ethyl methyl sulfone (EMS)	From methanethiol and bromoethane			✓
		From ethanethiol and chloromethane			✓

Most of the solvent production processes described in Ecoinvent are based on generic data. For instance, flows like energy used or transport of reactants are based on average data for the production of organic chemicals. In order to be consistent with these inventories, we have used generic data when we could not find specific information about the process. Thus, we first describe the LCI of the production process of a generic solvent. Unless stated otherwise, the values presented here will be used for the development of new LCI.

2.1. Production of a generic solvent

The production process of a generic solvent is based on the production processes for GBL, THF, DME and EA described in Ecoinvent [1] and illustrated in Figure 1. In the subsequent description, names in *italics* correspond to Ecoinvent flows.

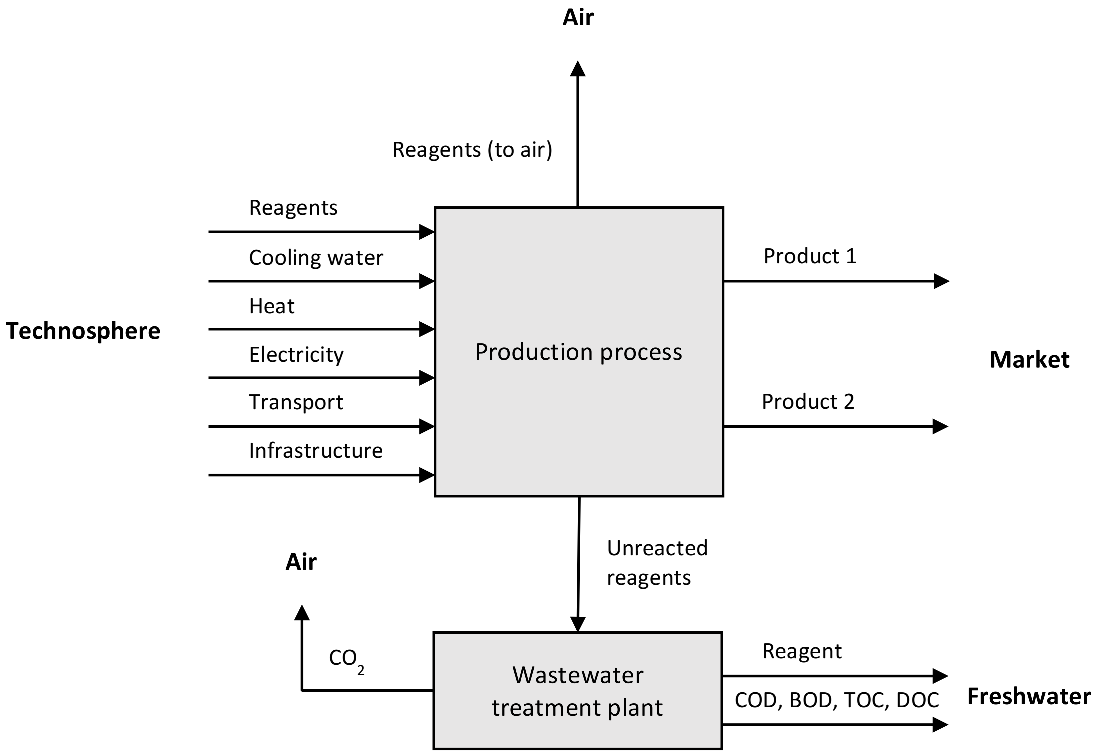


Figure 1Production process of a generic solvent, based on [1]

We assume a conversion rate of 95% and a selectivity of 100% for a molar yield of 95%. 0.2% of the reagents are supposed to be emitted to air, and 4.8% to the wastewater, which is subsequently treated in a wastewater treatment plant (WWTP) with a removal efficiency of 90% (Table 2). These values are common in a number of Ecoinvent processes for the production of solvents and other organic substances.

Table 2 Process information for the production of a generic solvent

Conversion	95%
Reagent to air	0.2%
Reagent to WWT	4.8%
Removal efficiency of the WWTP	90%

We considered reagent recycling as part of the production process and thus, we did not modelled explicitly. The conversion rate presented in Table 2 and subsequent conversions are not necessarily the rates of a one-step reaction, but the overall conversion efficiency of a process that might include several stages with or without recirculation.

For processes with a different conversion, the fraction of reagents entering the WWTP can be calculated as follow:

$$Reagent\ to\ WWTP = 100\% - Conversion - Reagent\ to\ air$$

If the reagent is a gas, we assume that the non-reacting fraction is completely emitted to air. Such assumption is consistent with Ecoinvent inventories where no specific information on emissions was available e.g. fate of hydrogen during Butene hydroformylation[1].

2.1.1. Infrastructure

The default plant for the production of solvents in Ecoinvent, *chemical factory, organics – GLO,* has an average output of 50,000 tons end product/year and a lifespan of 50 years. Thus, we assumed 4.00E-10 plants (units) per kg of solvent produced.

2.1.2. Raw materials and auxiliaries

The amount of reagents required is function of the conversion, the selectivity rates and stoichiometry of the reaction as well as of the molecular weights of the compounds involved. For the production of 1kg of solvent and related products, 24 kg of *Water, cooling, unspecified origin* are used.

2.1.3. Energy

The default Ecoinvent plant requires 3.2 MJ/kg product split into 50% natural gas, 38% electricity and 12% steam from external sources, which is also assumed to come from natural gas. Since we assumed the plant to be located in the EU—without specifying the state— it requires 2 MJ of *heat, district or industrial, natural gas | heat production, natural gas, at industrial furnace > 100kW – Europe without Switzerland and 0.33 kWh of electricity, medium voltage | market group for electricity – Europe without Switzerland.*

2.1.4. Transportation

We used the standard distances of 100 km for *transport, freight, lorry, unspecified* and 600 km for *transport, freight train – Europe without Switzerland* for those reagents not coming from a market activity[1].

2.1.5. Emissions to air

As already mentioned, we assumed 0.2% of the reagents are emitted to air "from the purge vent, the distillation vent and fugitive emissions" as in [1]. Also, *Carbon dioxide, fossil* will be emitted to air as a result of the removal of reagents from the wastewater (see below).

2.1.6. Emissions to water

As in [1], we assumed the remaining fraction of unreacted reagent (4.8% for a generic solvent) to leave the production process with the wastewater. The latter is treated in a dedicated WWTP with a removal efficiency of 90%. This is the efficiency of all WWTP described in the Ecoinvent processes mentioned in Table 1, and is within the ranges reported for the removal of organosulfur compounds [2]. The carbon contained in the removed reagent is emitted to air as *Carbon dioxide, fossil* and calculated according to the following equation:

$$C_wH_xO_yS_z + \left(\frac{2w + x - y}{2}\right) O_2 \rightarrow wCO_2 + \frac{x}{2} H_2O + zS$$

The remaining reagent is emitted to water. Its carbon content is used to calculate the *COD, Chemical Oxygen Demand; BOD, Biological Oxygen Demand; TOC, Total Organic Carbon;* and *DOC, Dissolved Organic Carbon* according to the assumptions presented in Table 3.

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[1] For a given product, a market activity in Ecoinvent includes an average of the different sources from where the product comes from i.e. different production processes or geographical locations as well as an average transport. (http://www.ecoinvent.org/support/faqs/methodology-of-ecoinvent-3/what-is-a-market-and-how-is-it-created.html)

Table 3 Carbon content of the remaining reagent in water

COD (kg)	$= 0.96 \cdot \frac{\left(\frac{2w+x-y}{2}\right) \cdot M_{O_2}}{M_{reagent}} \cdot m_{remaining\ reagent}(kg)$
BOD(kg)	=COD
TOC (kg)	$= \frac{w \cdot M_C}{M_{reagent}} \cdot m_{remaining\ reagent}(kg)$
DOC (kg)	=TOC

Note that the four parameters measure the same magnitude, the content of carbon in water, and including all of them will most likely overestimate the Eutrophication impact of the process.

Since Ecoinvent 3.0, it is possible to conduct mass, carbon, and water balances [3]. For the latter, and in consistence with other Ecoinvent processes, the 0.024 m^3 of cooling water entering the process are assumed to leave it, 0.0147 m3 as *Water, to water, unspecified* and the remaining $0.0093m^3$ as *Water, to air, unspecified.*

2.1.7. Life Cycle Inventory

The LCI of the production process of a generic solvent is presented in Table 4

Table 4 LCI of the production process of 1 kg of a generic solvent

	Inputs	
Infrastructure	Industrial plant (u)	4.88E-10
Raw materials and auxiliaries	Reagent 1 (kg)	Variable
	Reagent 2 (kg)	Variable
	Water (m^3)	2.00E+00
Energy	Heat (MJ)	3.30E-01
	Electricity (kWh)	2.40E-02
Transport	Truck 32 ton (km)	1.00E+02
	Train (km)	5.00E+02
	Outputs	
Products	Product (kg)	0.00E+00
Emissions to air	Water (kg)	9.30E+00
	Reagent 1 (kg)	2.00E-03
	Reagent 2 (kg)	2.00E-03
	CO_2 from WWT (g)	Variable
Emissions to water	Reagent 1 (kg)	10% of input to WWTP
	Reagent 2 (kg)	10% of input to WWTP
	COD (g)	Variable
	BOD (g)	Variable
	TOC (g)	Variable
	DOC (g)	Variable
	Water (m^3)	1.47E-02

3. Production of GBL

3.1. Reppe process

The Life Cycle Inventory for the production of GBL through the dehydrogenation of 1,4-butanediol (Reppe process) is already included in the Ecoinvent database [1]. All flows in the LCI follows the procedure described in 2.1.

3.2. Maleic anhydride pathway

The hydrogenation of maleic anhydride can be described according to the following reaction:

$$\underset{\text{Maleic Anhydride}}{C_4H_2O_3} + 3H_2 \rightarrow \underset{\text{GBL}}{C_4H_6O_2} + H_2O$$

GBL can be further hydrogenated to THF:

$$C_4H_6O_2 + 2H_2 \rightarrow \underset{\text{THF}}{C_4H_8O} + H_2O$$

According to US patent 2,772,291 [4], the maximum GBL molar yield is 60% together with 9% THF (Table 5). The non-reacting fraction of maleic anhydride is split between emissions to air and to water as explained in section 2.1. As a gas, we assume all non-reacting hydrogen is emitted to air.

Table 5 Efficiency of the hydrogenation of maleic anhydride for the production of GBL and additional process information.

Process efficiency

Conversion	69%	
	GBL	THF
Selectivity	87%	13%
Molar yield	60%	9%
Yield (kg/kg maleic anhydride)	0.527	0.066

Additional process information

Maleic anhydride (emissions to air)	0.2%
Maleic anhydride (to WWTP)	30.8%
Hydrogen (emissions to air)	31.0%

3.2.1. Infrastructure

See 2.1.1

3.2.2. Raw materials and auxiliaries

The two reagents required for the process are *market for hydrogen, liquid [RER]* and *market for maleic anhydride.* Two different routes for the production of maleic anhydride are available in Ecoinvent: *maleic anhydride production by catalytic oxidation of benzene [RER]*(representing 20% of the market), and *by direct oxidation of n-butane [RER]*(representing the remaining 80% of the market). If the maleic anhydride has to be synthesized in situ, or if one exclusive supplier is desired, the LCI should be changed accordingly, because they present very different environmental profiles.

3.2.3. Energy

See 2.1.3

3.2.4. Transportation

Since both reagents are available as market activities, no transport is required.

3.2.5. Emissions to air

See 2.1.5

3.2.6. Emissions to water

As for 2.1.6 and 3.2., 30.8% of maleic anhydride ends up in the WWTP, where it is removed with an efficiency of 90% according to the following reaction.

$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$

3.2.7. Life Cycle Inventory

The LCI for the production of 1 kg GBL is presented in Table 6

Table 6 Life cycle inventory of the hydrogenation of maleic anhydride for 1 Kg production of GBL

	Inputs	
Infrastructure	Industrial plant (u)	4.50E-10
Raw materials and auxiliaries	Maleic anhydride (kg)	1.38E+00
	Hydrogen (kg)	9.17E-02
	Water (m^3)	2.70E-02
Energy	Heat (MJ)	2.25E+00
	Electricity (kWh)	3.71E-01
	Outputs	
Products	GBL (kg)	1.00E+00
Emissions to air	Water (kg)	1.05E+01
	Maleic anhydride (kg)	2.76E-03
	Hydrogen (kg)	4.59E-03
	CO_2 from WWT (kg)	1.07E-01
Emissions to water	Maleic anhydride (kg)	6.62E-03
	COD (kg)	6.22E-03
	BOD (kg)	6.22E-03
	TOC (kg)	3.24E-03
	DOC (kg)	3.24E-03
	Water (m^3)	1.65E-02

4. Production of THF

4.1. Reppe process

The Life Cycle Inventory for the production of THF from acetylene and formaldehyde (Reppe process) is already included in the Ecoinvent database [1]. Energy is process specific, but the rest of flows follows what we described in 2.1.

4.2. Maleic anhydride pathway

As seen in 3.2, the hydrogenation of maleic anhydride can lead to the formation of THF according to the following reaction:

$$C_4H_2O_3 + 5H_2 \rightarrow C_4H_8O + 2H_2O$$

A theoretical plant for the production of 5000 metric tons THF per year is described in [6], which we use to generate the LCI. The plant is expected to produce 5000 metric tons/year of THF operating 333 days/year. It requires 8000 metric tons of maleic anhydride and 9700 Nm^3/year pure hydrogen. The non-reacting fraction of maleic anhydride is split between emissions to air and to water. As a gas, we assume all non-reacting hydrogen is emitted to air (Table 7).

Table 7 Efficiency of the hydrogenation of maleic anhydride for the production of THF and additional process information.

Process efficiency	
Conversion	85%
	THF
Selectivity	100%
Molar yield	85%
Yield (kg/kg maleic anhydride)	0.627
Additional process information	
Maleic anhydride (emissions to air)	0.2%
Maleic anhydride (to WWTP)	14.6%
Hydrogen (emissions to air)	14.8%

4.2.1. Infrastructure

We assumed the same lifespan for the plant in [6] as the one in 2.1. (50 years) but kept the 5000 tons per year described in the original reference.

4.2.2. Raw materials and auxiliaries

The same reagents as for the production of GBL via maleic anhydride (3.2.2) were used.

4.2.3. Energy

Kataneka et al. estimated $1.25 \cdot 10^3$ kcal/h of Fuel gas and 336 kWh/h electricity would be required. The same processes as in 2.1.3 were used.

4.2.4. Transportation

Since both reagents are available as market activities, no transport is required.

4.2.5. Emissions to air

See 2.1.5

4.2.6. Emissions to water

As per 2.1.6 and4.2, 14.6% of maleic anhydride ends up in the WWTP, where it is removed with an efficiency of 90% according to the following reaction.

$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$

4.2.7. Life Cycle Inventory

The LCI of the hydrogenation of maleic anhydride for the production of 1kg of THF in Table 8 for the original process, and in Table 9 for the optimized process.

Table 8 Life cycle inventory of the hydrogenation of maleic anhydride for the production of 1kg of THF

	Inputs	
Infrastructure	Industrial plant (u)	4.00E-09
Raw materials and auxiliaries	Maleic anhydride (kg)	1.60E+00
	Hydrogen (kg)	3.46E-02
	Water (m^3)	5.03E-05
Energy	Heat (MJ)	8.36E-03
	Electricity (kWh)	5.85E-01
	Outputs	
Products	THF (kg)	1.00E+00
Emissions to air	Water (kg)	9.30E+00
	Maleic anhydride (kg)	3.19E-03
	Hydrogen (kg)	6.89E-03
	CO_2 from WWT (kg)	3.76E-01
Emissions to water	Maleic anhydride (kg)	2.32E-02
	COD (kg)	2.19E-02
	BOD (kg)	2.19E-02
	TOC (kg)	1.14E-02
	DOC (kg)	1.14E-02
	Water (m^3)	1.47E-02

Table 9 Life cycle inventory of the hydrogenation of maleic anhydride for the production of 1kg of THF (optimized)

	Inputs	
Infrastructure	Industrial plant (u)	4.00E-09
Raw materials and auxiliaries	Maleic anhydride (kg)	1.43E+00
	Hydrogen (kg)	2.92E-02
	Water (m^3)	5.03E-05
Energy	Heat (MJ)	8.36E-03
	Electricity (kWh)	5.85E-01
	Outputs	
Products	THF (kg)	1.00E+00
Emissions to air	Water (kg)	9.30E+00
	Maleic anhydride (kg)	2.86E-03
	Hydrogen (kg)	1.46E-03

	CO_2 from WWT (kg)	1.11E-01
Emissions to water	Maleic anhydride (kg)	6.87E-03
	COD (kg)	6.46E-03
	BOD (kg)	6.46E-03
	TOC (kg)	3.37E-03
	DOC (kg)	3.37E-03
	Water (m^3)	1.47E-02

4.3. Mitsubishi Acetoxylation

The production of THF through the Mitsubishi Acetoxylation consists of three stages (Figure 2).

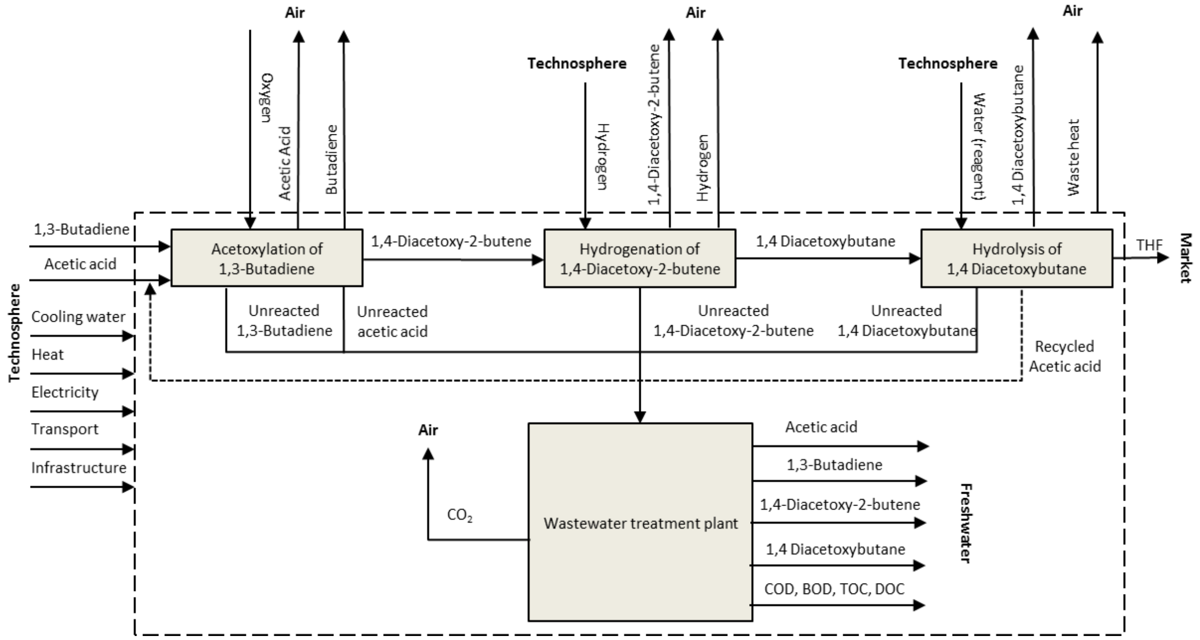

Figure 2 Production process of THF through Mitsubishi Acetoxylation

The reaction of 1,3-Butadiene with acetic acid in oxidizing conditions results in the production of 1,4-Diacetoxy-2-butene following the reaction below. At 70°C and 70 bars, the reaction has a selectivity of 90% according to [6].

$$C_4H_6 + 2C_2H_4O_2 + \frac{1}{2}O_2 \rightarrow C_8H_{12}O_4 + H_20$$

The subsequent hydrogenation process has a 98% selectivity for 1,4-Diacetoxybutane at 60°C and 50 bars in the presence of a Pb/C catalyst: complete the reaction

$$C_8H_{12}O_4 + H_2 \rightarrow C_8H_{14}O_4$$

The final hydrolysis with acidic exchange resin has a 90% selectivity for THF. The resulting acetic acid is recycled back to the first stage.

$$C_8H_{14}O_4 + 2H_2O \rightarrow C_4H_8O{+}2C_2H_4O_2{+}2C_4H_{10}O_2$$

Because the reviewed literature did not include conversion rates for any of the aforementioned reactions, we assumed it to be 95% as in 2.1.

No byproducts were specified except for the hydrolysis stage, where 1,4-Butanediol is produced to which we allocated the 10% remaining selectivity. As in 2.1 Inventories are scaled for the final production of 1kg of solvents.

Table 10 Efficiency of the different stages of the Mitsubishi acetoxylation and additional process information.

Process efficiency				
	Stage 1	Stage 2	Stage 3	
Reagent	*1,3 butadiene*	*1,4-Diacetoxy-2-butene*	*1,4-Diacetoxybutane*	
Conversion	95%	95%	95%	
Product	*1,4-Diacetoxy-2-butene*	*1,4-Diacetoxybutane*	*THF*	*Butanediol*
Selectivity	90%	98%	90%	10%
Molar yield	85.5%	93.1%	85.5%	9.5%
Yield (kg/kg)	2.722	0.942	0.354	0.098
Additional process information				
Emission to air	0.2%	0.2%	0.2%	
To WWTP	4.8%	4.8%	4.8%	

4.3.1. Infrastructure

As in 2.1.1, since intermediates are not considered part of the plant's final production.

4.3.2. Raw materials and auxiliaries

The two reagents required for the first step are *marketed for butadiene [GLO]* and *marketed for acetic acid, without water in 98% solution [GLO].* No consumption of oxygen (or air) was allocated to the process, in agreement with other oxidation processes described in Ecoinvent (e.g. acetaldehyde oxidation, butane oxidation, dimethyl sulfoxide, propylene ammoxidation)[1].For the second step, the reagent required is *marketed for hydrogen, liquid [RER],* and for the third stage, *marketed for water, deionized, from tap water, at user [GLO],*in consistency with other hydrolysis processes (e.g. Benzyl alcohol)[1].

4.3.3. Energy

No information was found concerning the energy requirements for the Mitsubishi acetoxylation. As a result, we allocate the same energy requirements as in 2.1.3 to each of the three stages.

4.3.4. Transportation

Since all reagents are available as market activities, no transport is required.

4.3.5. Emissions to air

See 2.1.5

4.3.6. Emissions to water

As per 2.1.6 and4.3, 4.8% of all organic reagents end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$1,3-\text{Butadiene: } C_4H_6+\frac{11}{2}O_2 \rightarrow 4CO_2+3H_2O$$

$$\text{Acetic Acid: } C_4H_4O_2+2O_2 \rightarrow 2CO_2+2H_2O$$

$$1{,}4-\text{Diacetoxy}-2-\text{butene: } C_8H_{12}O_4+9O_2\rightarrow 8CO_2+6H_2O$$

$$1{,}4-\text{Diacetoxybutane: } C_8H_{14}O_4+\frac{19}{2}O_2\rightarrow 8CO_2+7H_2O$$

4.3.7. Life Cycle Inventory

The LCI for the production of 1 kg of THF is presented in Table 11.

Table 11Life cycle inventory of the Mitsubishi acetoxylation for the production of 1kg of solvents

	Inputs	
Infrastructure	Industrial plant (u)	5.11E-10
Raw materials and auxiliaries	1,3 butadiene (kg)	1.10E+00
	Acetic acid (kg)	4.36E-01
	Hydrogen (kg)	3.70E-02
	Air (m3)	1.30E+00
	Cooling water (m3)	1.70E-01
	Process water (kg)	3.28E-01
Energy	Heat (MJ)	1.42E+01
	Electricity (kWh)	2.35E+00
	Outputs	
Products	THF	1.00E+00
Emissions to air	Water (kg)	6.61E+01
	1,3 butadiene (kg)	2.20E-03
	Acetic acid (kg)	4.18E-03
	Hydrogen (kg)	1.74E-03
	1,4-Diacetoxy-2-butene (kg)	6.00E-03
	1,4-Diacetoxybutane (kg)	5.65E-03
	CO_2 from WWT (kg)	8.00E-01
Emissions to water	1,3 butadiene (kg)	5.29E-03
	Acetic acid (kg)	1.00E-02
	1,4-Diacetoxy-2-butene (kg)	1.44E-02
	1,4-Diacetoxybutane (kg)	5.65E-03
	COD (kg)	7.58E-02
	BOD (kg)	7.58E-02
	TOC (kg)	2.42E-02
	DOC (kg)	2.42E-02
	Water (m3)	1.20E-01

5. Production of DME

5.1. Cleavage of ethylene oxide in presence of dimethyl ether

The Life Cycle Inventory for the production of DME from ethylene oxide and dimethyl ether is already included in the Ecoinvent database [1]. Everything is as described in 2.1.

5.2. DOW process

The DOW process for the production of glyme glycol diethers consists of two stages[7]:

1) The reaction of ethylene oxide with an alcohol for the production of a glycol monoether.
2) A Williamson synthesis: the reaction of the glycol monoether with sodium to produce a sodium alkoxide, which further reacts with an alkyl halide to produce the glyme.

None of these stages are included in Ecoinvent for the production of ethylene glycol monomethyl ether (EGME) and the further synthesis of DME. Nevertheless, both stages are present for the production of ethylene glycol monoethyl ether (EGEE) and ethylene glycol diethyl ether. Thus, we selected *ethylene glycol diethyl ether production [RER]* as a proxy for the production of DME through the DOW process.

5.3. Shell Omega process

This processes starts with the production of EC from ethylene oxide and carbon dioxide[8], a process included in Ecoinvent.

The subsequent opening of the EC ring with methanol at 150-200°C and 80 bars catalyzed with Zirconium (IV) acetylacetonate results in ethylene glycol. Jagtap *et al* reported a conversion of 96% for EC, we assumed the same for MeOH for a 75% molar yield of ethylene glycol.

$$C_3H_4O_3 + CH_3OH \rightarrow C_2H_6O_2$$

The final stage is the further addition/coupling of methanol at 160-220°C using a polyperfluorosulfonic acid resin as catalyst. According to [9], 76% of the Ethylene glycol reacts and we assumed the same fraction for MeOH for a final molar yield of 21.3% in DME and 50% in EGME, another solvent.

$$C_2H_6O_2 + 2CH_3OH \rightarrow C_4H_{10}O_2 + H_2O$$

Table 12 Efficiency of the different stages of the Shell Omega process and additional process information.

Process efficiency			
	Stage 2	Stage 3	
Reagent	*EC*	*Ethylene glycol*	
Conversion	96.0%	76%	
Product	*Ethylene glycol*	*DME*	*EGME*
Selectivity	78%	28.1%	66.1%
Molar yield	75%	21.3%	50.0%
Yield (kg/kg)	0.53	0.31	0.61
Additional process information			
Emission to air	0.2%	0.2%	
To WWTP	3.8%	24.1%	

5.3.1. Infrastructure

As in 2.1.1

5.3.2. Raw materials and auxiliaries

Since the production of ethylene carbonate is considered part of the Shell Omega process, we used *ethylene carbonate production [RoW]* as source for EC. Methanol on the other hand, is not considered to be manufactured in situ, thus we selected *market for methanol, from synthetic gas* as its source.

5.3.3. Energy

No information was available on the energy consumption of the different stages. Thus, we proceeded as in 2.1.3

5.3.4. Transportation

Since ethylene carbonate is produced in situ and methanol is available as a as market activity, no transport is required.

5.3.5. Emissions to air

See 2.1.5

5.3.6. Emissions to water

As per 2.1.6 and5.3., 3.8% of the EC and of methanol from the second stage and 24.1% of ethylene glycol and of methanol end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$Ethylene\ carbonate: (CH_2O)_2CO + \frac{5}{2}O_2 \rightarrow 3CO_2 + 2H_2O$$

$$Methanol: CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

5.3.7. Life Cycle Inventory

The LCI of the production process of 1 kg of solvents is presented in Table 13 for the original process and in Table 14 for the optimized process.

Table 13 Life Cycle inventory of the Shell Omega process for the production of 1kg of DME

	Inputs	
Infrastructure	Industrial plant (u)	1.19E-09
Raw materials and auxiliaries	Ethylene carbonate (kg)	5.64E+00
	Methanol (kg)	3.46E+00
	Water (m^3)	1.43E-01
Energy	Heat (MJ)	1.19E+01
	Electricity (kWh)	1.97E+00
	Outputs	
Products	DME (kg)	1.00E+00
Emissions to air	Water (kg)	5.55E+01
	Ethylene carbonate (kg)	1.13E-02
	Methanol (kg)	6.93E-03
	Ethylene glycol (kg)	6.47E-03
	CO_2 from WWT (kg)	1.51E+00
Emissions to water	Ethylene carbonate (kg)	2.14E-02
	Methanol (kg)	4.18E-02
	Ethylene glycol (kg)	7.80E-02
	COD (kg)	1.83E-01
	BOD (kg)	1.83E-01
	TOC (kg)	5.47E-02
	DOC (kg)	5.47E-02
	Water (m^3)	8.77E-02

Table 14 Life Cycle inventory of the Shell Omega process for the production of 1kg of DME (optimized)

	Inputs	
Infrastructure	Industrial plant (u)	1.19E-09
Raw materials and auxiliaries	Ethylene carbonate (kg)	5.64E+00
	Methanol (kg)	3.18E+00
	Water (m^3)	1.43E-01
Energy	Heat (MJ)	1.19E+01
	Electricity (kWh)	1.97E+00
	Outputs	
Products	DME (kg)	1.00E+00
Emissions to air	Water (kg)	5.55E+01
	Ethylene carbonate (kg)	1.13E-02
	Methanol (kg)	6.36E-03
	Ethylene glycol (kg)	5.15E-03
	CO_2 from WWT (kg)	3.21E-01
Emissions to water	Ethylene carbonate (kg)	2.14E-02
	Methanol (kg)	1.32E-02
	Ethylene glycol (kg)	1.24E-02
	COD (kg)	5.52E-02
	BOD (kg)	5.52E-02
	TOC (kg)	1.85E-02
	DOC (kg)	1.85E-02
	Water (m^3)	8.77E-02

5.4. Hydration/coupling pathway

The coupling of ethylene glycol and methanol has already been described as *stage 3* in section 5.3[9]. However, the ethylene glycol can be produced through an alternative pathway, hydrating ethylene oxide. This is the process included in Ecoinvent for the production of ethylene glycol.

5.4.1. Infrastructure

As in 2.1.1

5.4.2. Raw materials and auxiliaries

As in 5.3.2, *market for methanol, from synthetic gas* was used as a source for methanol. For Ethylene glycol, we selected *market for ethylene glycol [GLO].*

5.4.3. Energy

No information was available on the energy consumption at the different stages. Thus, we proceeded as in 2.1.3

5.4.4. Transportation

Since all reagents are available as market activities, no transport is required.

5.4.5. Emissions to air

See 2.1.5

5.4.6. Emissions to water

As in 5.3.6 24.1% of ethylene glycol and methanol end up in the wastewater treatment plant, where they are removed with an efficiency of 90% according to the following reactions:

$$Ethylene\ glycol: C_2H_6O_2 + \frac{5}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$Methanol: CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

5.4.7. Life Cycle Inventory

The LCI for the production process of 1 kg of DME through the hydration/coupling pathway presented in Table 15 for the original process and in Table 16 for the optimized.

Table 15 Life Cycle inventory of the hydration/coupling process for the production of 1kg of DME

	Inputs	
Infrastructure	Industrial plant (u)	1.19E-09
Raw materials and auxiliaries	Ethylene glycol (kg)	3.23E+00
	Methanol (kg)	1.41E+00
	Water (m³)	7.16E-02
Energy	Heat (MJ)	5.96E+00
	Electricity (kWh)	9.84E-01
	Outputs	
Products	DME (kg)	1.00E+00
Emissions to air	Water (kg)	2.77E+01
	Ethylene glycol (kg)	6.47E-03
	Methanol (kg)	2.82E-03
	CO_2 from WWT (kg)	1.42E+00
Emissions to water	Ethylene glycol (kg)	7.80E-02
	Methanol (kg)	3.40E-02
	COD (kg)	1.52E-01
	BOD (kg)	1.52E-01
	TOC (kg)	4.30E-02
	DOC (kg)	4.30E-02
	Water (m³)	4.38E-02

Table 16 Life cycle inventory of the hydration/coupling process for the production of 1kg of DME (optimized)

	Inputs	
Infrastructure	Industrial plant (u)	1.19E-09
Raw materials and auxiliaries	Ethylene glycol (kg)	2.58E+00
	Methanol (kg)	1.13E+00
	Water (m^3)	7.16E-02
Energy	Heat (MJ)	5.96E+00
	Electricity (kWh)	9.84E-01
	Outputs	
Products	DME (kg)	1.00E+00
Emissions to air	Water (kg)	2.77E+01
	Ethylene glycol (kg)	5.15E-03
	Methanol (kg)	2.25E-03
	CO_2 from WWT (kg)	2.25E-01
Emissions to water	Ethylene glycol (kg)	1.24E-02
	Methanol (kg)	5.40E-03
	COD (kg)	2.41E-02
	BOD (kg)	2.41E-02
	TOC (kg)	6.81E-03
	DOC (kg)	6.81E-03
	Water (m^3)	4.38E-02

6. Production of Sulfolane

6.1. Hydrogenation of sulfolene

The production of sulfolane is a two stage process involving first the production of sulfolene from 1,3-Butadiene and sulfur dioxide at 70°C and 15 bar [10]. According to the same source, 94.95% conversion of butadiene is achieved with almost no impurities. SO_2 is used in excess and the non-reacting fraction is recirculated. Still, we assumed that a minimum of 0.2% if is lost as emission to air.

$$C_4H_6 + SO_2 \rightarrow C_4H_6O_2S$$

Following again [10], 95% of the sulfolene produced, reacts to produce pure sulfolane.

$$C_4H_6SO_2 + H_2 \rightarrow C_4H_8SO_2$$

The characteristics of the process detailed in Table 17 follow the general assumptions described in 2.1

Table 17 Efficiency of the different stages for the production of sulfolane and additional process information.

Process efficiency				
	Stage 1		*Stage 2*	
Reagent	*1,3-Butadiene*	*SO_2*	*Sulfolene*	*H_2*
Conversion	94.95%	99.80%	95.00%	95.00%
Product	*Sulfolene*		*Sulfolane*	
Selectivity	100.00%	100.00%	100.00%	100.00%
Molar yield	94.95%	94.95%	95.00%	95.00%
Yield (kg/kg)	2.07	1.75	0.97	57.08
Additional process information				
Emission to air	0.20%	0.20%	0.20%	5.00%
To WWTP	4.85%	0.00%	4.80%	0.00%

6.1.1. Infrastructure

As in 2.1.1, since intermediates are not considered part of the plant's final production.

6.1.2. Raw materials and auxiliaries

We selected the Ecoinvent processes *market for butadiene [GLO]* and *market for sulfur dioxide, liquid [RER]* for the two reagents required in the first stage and *market for hydrogen, liquid [RER],* for the hydrogen required in the second one.

6.1.3. Energy

No information was available on the energy consumption at the different stages. Thus, we proceeded as in 2.1.3

6.1.4. Transportation

Since all reagents are available as market activities, no transport is required.

6.1.5. Emissions to air

See 2.1.5

6.1.6. Emissions to water

As for 2.1.6 and Table 17, 4.85% of the 1,3-butadiene from the first stage and 4.8% of sulfolene from the second stage end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$1{,}3-\text{Butadiene}: C_4H_6+\frac{11}{2}O_2\rightarrow 4CO_2+3H_2O$$

$$Sulfolene: C_4H_6SO_2+5O_2\rightarrow 4CO_2+4H_2O$$

6.1.7. Life Cycle Inventory

The LCI of the production of 1 kg of sulfolane is presented in Table 18.

Table 18 Life cycle inventory of the production of 1kg of sulfolane

	Inputs	
Infrastructure	Industrial plant (u)	4.00E-10
Raw materials and auxiliaries	1,3-Butadiene (kg)	4.82E-01
	SO_2 (kg)	5.71E-01
	H_2 (kg)	1.75E-02
	Water (m^3)	4.80E-02
Energy	Heat (MJ)	4.00E+00
	Electricity (kWh)	6.60E-01
	Outputs	
Products	Sulfolane (kg)	1.00E+00
Emissions to air	Water (kg)	1.86E+01
	1,3-Butadiene (kg)	9.64E-04
	Sulfolene(kg)	2.07E-03
	H_2 (kg)	8.76E-04
	CO_2 from WWT (kg)	1.34E-01
Emissions to water	1,3-Butadiene (kg)	2.34E-03
	Sulfolene(kg)	4.97E-03
	COD (kg)	1.42E-02
	BOD (kg)	1.42E-02
	TOC (kg)	4.06E-03
	DOC (kg)	4.06E-03
	Water (m^3)	2.94E-02

7. Production of EMS

7.1. From methanethiol and bromoethane

EMS can be synthesized from methanethiol and bromoethane through the oxidation of the intermediate methyl thioethane.

Neither bromoethane or methanethiol are available in Ecoinvent. The latter can be synthesized via the reaction of methanol and hydrogen sulfide using Alumina-K_2WO_4 as catalyst according to [11] achieving both high conversion and high selectivity (stage 0 in

):

Process efficiency

	Stage 0			Stage 1	Stage 2
Reagent	*Methanol*			*Methanethiol*	*Methylthioethane*
Conversion	92.70%			95.00%	99.00%
Product	*CH3SH*	*$(CH3)_{2S}$*	*$(CH3)_{2O}$*	*Methylthioethane*	*EMS*
Selectivity	98.10%	1.00%	0.90%	100%	100%
Molar yield	90.94%	0.93%	0.83%	95.00%	99.00%
Yield (kg/kg)	1.37	0.01	0.01	1.50	1.41
Additional process information					
Emission to air	0.2%			0.2%	0.2%
To WWTP	7.1%			4.8%	0.8%

Methyl thioethane is produced by the reaction of an aqueous alkaline solution of methanethiol and bromoethane[12]. We could not find any information regarding the molar yields of the following reaction. Thus, we assumed 95% conversion and 100% selectivity as in 2.1 for both methanol and hydrogen sulfide (stage 1 in

Methyl thioethane is produced by the reaction of an aqueous alkaline solution of methanethiol and bromoethane[12]. We could not find any information regarding the molar yields of the following reaction. Thus, we assumed 95% conversion and 100% selectivity as in 2.1 for both methanol and hydrogen sulfide (stage 1 in

$$CH_3SH + C_2H_5Br \rightarrow C_3H_8S + \mathrm{HBr}$$

).

Process efficiency

	Stage 0			Stage 1	Stage 2
Reagent	*Methanol*			*Methanethiol*	*Methylthioethane*
Conversion	92.70%			95.00%	99.00%
Product	*CH3SH*	*$(CH3)_{2S}$*	*$(CH3)_{2O}$*	*Methylthioethane*	*EMS*
Selectivity	98.10%	1.00%	0.90%	100%	100%
Molar yield	90.94%	0.93%	0.83%	95.00%	99.00%
Yield (kg/kg)	1.37	0.01	0.01	1.50	1.41
Additional process information					
Emission to air	0.2%			0.2%	0.2%
To WWTP	7.1%			4.8%	0.8%

Methyl thioethane is oxidized with H_2O_2 in the presence of methanol and a

Na_2WO_4catalyst [13]. A 99% molar yield was reported, for which we assume 99% conversion and 100% selectivity (stage 2 in

).

$$C_3H_8S + H_2O_2 \rightarrow C_3H_8SO_2$$

Table 19
the different production of additional information.

Efficiency of stages for the EMS and process

Process efficiency

		Stage 0		Stage 1	Stage 2
Reagent		*Methanol*		*Methanethiol*	*Methylthioethane*
Conversion		92.70%		95.00%	99.00%
Product	*CH3SH*	*$(CH3)_{2S}$*	*$(CH3)_{2O}$*	*Methylthioethane*	*EMS*
Selectivity	98.10%	1.00%	0.90%	100%	100%
Molar yield	90.94%	0.93%	0.83%	95.00%	99.00%
Yield (kg/kg)	1.37	0.01	0.01	1.50	1.41

Additional process information

Emission to air	0.2%		0.2%	0.2%

Process efficiency

		Stage 0		Stage 1	Stage 2
Reagent		*Methanol*		*Methanethiol*	*Methylthioethane*
Conversion		92.70%		95.00%	99.00%
Product	*CH_3SH*	*$(CH_3)_2S$*	*$(CH_3)_2O$*	*Methylthioethane*	*EMS*
Selectivity	98.10%	1.00%	0.90%	100%	100%
Molar yield	90.94%	0.93%	0.83%	95.00%	99.00%
Yield (kg/kg)	1.37	0.01	0.01	1.50	1.41

Additional process information

Emission to air	0.2%		0.2%	0.2%
To WWTP	7.1%		4.8%	0.8%

7.1.1. Infrastructure

We assumed methanethiol was produced in the same plant synthesizing EMS. Since intermediates are not considered part of the plant's final production, we used the same infrastructure as in 2.1.1.

7.1.2. Raw materials and auxiliaries

As in previous processes, we selected *market for methanol, from synthetic gas* as the source for methanol. We also selected *market for hydrogen sulfide [GLO]* and *market for hydrogen peroxide, without water, in 50% solution state [GLO]* for hydrogen sulfide and hydrogen peroxide respectively. Bromoethane was not available in Ecoinvent, neither was hydrobromic acid, one of its precursors. Thus, we used *market for ethylene bromide [GLO]* as a proxy.

7.1.3. Energy

Folkins and Millers estimated the costs of utilities for the production of methanethiol to be 0.44 euro/lb[11]. Using the prices for electricity in the industry for 1962 available at http://www.eia.gov/totalenergy/data/annual/showtext.cfm?t=ptb0810, we estimated that 0.88kWh/kg of methanethiol were required, which is virtually identical to the total energy (electricity and heat) assumed for generic processes. For the other two stages, no information was available on their energy consumption, so we proceeded as in 4.3.3.

7.1.4. Transportation

Since all reagents are available as market activities, no transport is required.

7.1.5. Emissions to air

See 2.1.5

7.1.6. Emissions to water

As per 2.1.6 and

, 7.1% of the methanol from the production of methanethiol, 4.8% methanethiol and bromoethene from the first stage and 0.8% of methyl thioethane from the second stage end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

Process efficiency

	Stage 0			Stage 1	Stage 2
Reagent	*Methanol*			*Methanethiol*	*Methylthioethane*
Conversion	92.70%			95.00%	99.00%
Product	*CH_3SH*	*$(CH_3)_2S$*	*$(CH_3)_2O$*	*Methylthioethane*	*EMS*
Selectivity	98.10%	1.00%	0.90%	100%	100%
Molar yield	90.94%	0.93%	0.83%	95.00%	99.00%
Yield (kg/kg)	1.37	0.01	0.01	1.50	1.41

Additional process information

	Stage 0	Stage 1	Stage 2
Emission to air	0.2%	0.2%	0.2%
To WWTP	7.1%	4.8%	0.8%

$$Methanol: CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

$$Methanethiol: CH_3SH + 2O_2 \rightarrow CO_2 + 2H_2O + S^0$$

$$Methylthioethane: C_3H_8SH + 5O_2 \rightarrow 3CO_2 + 4H_2O + S^0$$

$$Bromoethane: C_2H_5Br + \tfrac{13}{4}O_2 \rightarrow 2CO_2 + \frac{5}{2}H_2O + Br$$

0.8% of the hydrogen peroxide used in stage 2 is assumed to also end in the WWTP, but not removed.

7.1.7. Life Cycle Inventory

The LCI for the production of 1 kg of EMS is presented in

Table 20.

Table 20 Life Cycle inventory of the production of 1kg of EMS

	Inputs	
Infrastructure	Industrial plant (u)	4.00E-10
Raw materials and auxiliaries	Methanol	3.43E-01
	H_2S(kg)	3.60E-01
	Bromoethane (kg)	1.07E+00
	Hydrogen peroxide (kg)	6.35E-01
	Water (m^3)	5.24E-02
Energy	Heat (MJ)	4.37E+00
	Electricity (kWh)	7.26E-01
	Outputs	
Products	EMS (kg)	1.00E+00
	Dimethylsulfide	5.13E-03
Emissions to air	Water (kg)	2.03E+01
	Methanol (kg)	6.85E-04
	H_2S (kg)	2.63E-02
	Methaethiol (kg)	9.46E-04
	Bromoethane (kg)	2.14E-03
	Methylthioethane (kg)	1.42E-03
	Hydrogen peroxide (kg)	6.35E-04
	CO_2 from WWT (kg)	8.59E-02
Emissions to water	Methanol (kg)	2.43E-03
	Methaethiol (kg)	2.27E-03
	Bromoethane (kg)	5.14E-03
	Methylthioethane (kg)	5.69E-04
	Hydrogen peroxide (kg)	2.54E-03
	COD (kg)	1.12E-02
	BOD (kg)	1.12E-02
	TOC (kg)	2.60E-03
	DOC (kg)	2.60E-03
	Water (m^3)	3.21E-02

7.2. From ethanethiol and chloromethane

Similar to the previous route, EMS can also be synthesized from ethanethiol and chloromethane, In this case, the intermediate to be oxidized is ethyl thioethane.

Ethanethiol is not available in Ecoinvent, but it can be synthesized via the reaction of ethanol and hydrogen sulfide using Alumina-K_2WO_4 as catalyst in the same way as for methanethiol [11] (stage 0 in Table 21):

$$C_2H_5OH + H_2S \rightarrow C_2H_5SH$$

Methyl thioethane is produced by the reaction of an aqueous alkaline solution of ethanethiol and chloromethane[12]. As in 7.1 we assumed 95% conversion and 100% selectivity as in 2.1 for both methanol and hydrogen sulfide (stage 1 in Table 21).

$$C_2H_5SH + CHCl_3 \rightarrow C_3H_8S$$

As before methyl thioethane can also be oxidized with H_2O_2 in the presence of methanol and a Na_2WO_4catalyst [13]. As for methyl thioethane we assume 99% conversion and 100% selectivity (stage 2 in Table 21).

$$C_3H_8S + H_2O_2 \rightarrow C_3H_8SO_2$$

Table 21 Efficiency of the different stages for the production of EMS and additional process information.

		Process efficiency				
	Stage 0				Stage 1	Stage 2
Reagent	*Ethanol*				*Ethanethiol*	*Methylthioethane*
Conversion	83.40%				95.00%	99.00%
Product	*C_2H_5SH*	*$(C_2H_5)_2S$*	*$(C_2H_5)_2O$*	*C_2H_4*	*Methylthioethane*	*EMS*
Selectivity	82%	6%	9%	2%	100%	100%
Molar yield	68.72%	5.00%	7.76%	1.92%	95.00%	99.00%
Yield (kg/kg)	0.927	0.098	0.125	0.012	1.165	1.406
		Additional process information				
Emission to air	0.20%				0.20%	0.20%
To WWTP	16.40%				4.80%	0.80%

7.2.1. Infrastructure

We assumed ethanethiol was produced in the same plant synthesizing EMS. Since intermediates are not considered part of the plant's final production, we used the same infrastructure as in 2.1.1.

7.2.2. Raw materials and auxiliaries

We selected *market for ethanol, from synthetic gas* as the source for methanol. We also selected *market for hydrogen sulfide [GLO]* and *market for hydrogen peroxide, without water, in 50% solution state [GLO,* and *market for methyl chloride [GLO]* for hydrogen sulfide, hydrogen peroxide, and chloromethane respectively.

7.2.3. Energy

No information was available on their energy consumption, so we proceeded as in 4.3.3.

7.2.4. Transportation

Since all reagents are available as market activities, no transport is required.

7.2.5. Emissions to air

See 2.1.5

7.2.6. Emissions to water

As per 2.1.6 and Table 21, 16.4% of the ethanol from the production of ethanethiol, 4.8% ethanethiol and chloromethane from the first stage and 0.8% of methyl thioethane from the second stage end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$Ethanol: C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$Ethanethiol: C_2H_5SH + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O + S^0$$

$$Methylthioethane: C_3H_8SH + 5O_2 \rightarrow 3CO_2 + 4H_2O + S^0$$

0.8% of the hydrogen peroxide used in stage 2 is assumed to also end in the WWTP, but not removed.

7.2.7. Life Cycle Inventory

The LCI of the production of 1 kg of EMS is presented in Table 22.

Table 22 Life Cycle inventory of the production of 1kg of EMS

	Inputs	
Infrastructure	Industrial plant (u)	9.91E-10
Raw materials and auxiliaries	Ethanol (kg)	6.57E-01
	H_2S (kg)	1.39E+00
	Chloromethane (kg)	1.17E+00
	Hydrogen peroxide (kg)	1.59E-01
	Water (m^3)	5.94E-02
Energy	Heat (MJ)	4.95E+00
	Electricity (kWh)	8.17E-01
	Outputs	
Products	Ethyl methyl sulfone (kg)	1.00E+00
Emissions to air	Water (kg)	2.30E+01
	Ethanol (kg)	1.32E-03
	H_2S (kg)	9.07E-01
	Ethanethiol (kg)	1.22E-03
	Chloromethane (kg)	5.87E-02
	Methylthioethane (kg)	1.42E-03
	Hydrogen peroxide (kg)	6.35E-04
	CO_2 from WWT (kg)	2.32E-01
Emissions to water	Ethanol (kg)	1.08E-02
	Ethanethiol (kg)	2.93E-03
	Methylthioethane(kg)	5.69E-04

	Hydrogen peroxide (kg)	2.54E-03
	COD (kg)	2.90E-02
	BOD (kg)	2.90E-02
	TOC (kg)	7.04E-03
	DOC (kg)	7.04E-03
	Water (m^3)	3.64E-02

8. Production of DMC

8.1. Shell Omega process and methanol coupling

The production of dimethyl carbonate is not available in Ecoinvent. Nevertheless, Monteiro et al. modeled three processes HYSYS for the production of DMC [14]: From urea and two versions of the Shell Omega process. Of the latter two, the one with the lowest impact was also used by Dunn et al. for their MFA on Li-ion batteries [15]. We have also adapted Monteiro's process to build our Life Cycle Inventory.

As presented in Figure 3, the production of DMC is conducted in two steps starting with the synthesis of ethylene carbonate from ethylene oxide and atmospheric CO$_2$, followed by coupling with methanol for the production of DMC and ethylene glycol.

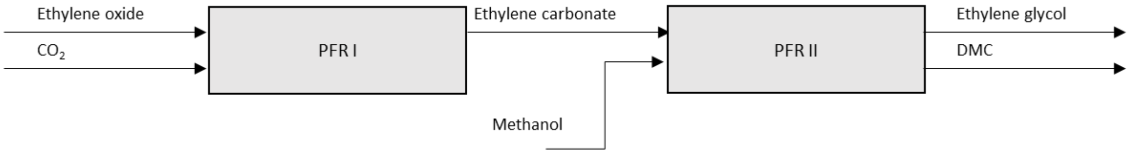

Figure 3 Production of *DMC and Ethylene glycol, adapted from [14]:*

Monteiro *et al*. achieved 100% conversion for both stages, which we decreased to 99% in consequence with 2.1.

8.1.1. Infrastructure

The plant simulated by Monteiro produced around 66900 and 97400 tons/year of ethylene glycol and DMC respectively. However, the fraction of industrial plant per kg of product is the same as in 2.1.1.

8.1.2. Raw materials and auxiliaries

We selected *market for ethylene oxide [GLO]* as the source of EO and *carbon dioxide, in air [natural resource/in air]* as the source of CO$_2$Monteiro et al considered the processes a temporary sink for CO$_2$.As in previous sections, we used *market for methanol, from synthetic gas* as the source for methanol.

8.1.3. Energy

Monteiro et al. estimated a net energy consumption of TJ/year, of which 93.5% would be heat. As per our calculations, this is equivalent to 1.23 MJ and 0.023 kWh per kg of products.

8.1.4. Transportation

Since all reagents are available as market activities, no transport is required.

8.1.5. Emissions to air

See 2.1.5

8.1.6. Emissions to water

As per 2.1.6, 0.8% of the ethylene oxide, ethylene carbonate and methanol used end up in the WWTP, where they are removed with 90% efficiency according to the following reactions:

$$Ethylene\ oxide: C_2H_4O + \frac{5}{2}O_2 \rightarrow 2CO_2 + 2H_2O$$

$$Ethylene\ carbonate: (CH_2O)_2CO + \frac{5}{2}O_2 \rightarrow 3CO_2 + 2H_2O$$

$$Methanol: CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

8.1.7. Life Cycle Inventory

The LCI of the production of 1 kg of DMC is presented in Table 23.

Table 23 Life Cycle inventory of the production of 1kg of DMC

	Inputs	
Infrastructure	Industrial plant (u)	9.82E-10
Raw materials and auxiliaries	Ethylene oxide (kg)	7.18E-01
	CO_2(kg)	7.25E-01
	Methanol (kg)	1.05E+00
	Water (m^3)	5.89E-02
Energy	Heat (MJ)	3.02E+00
	Electricity (kWh)	5.77E-02
	Outputs	
Products	DMC	1.00E+00
Emissions to air	Water (kg)	2.28E+01
	Ethylene oxide (kg)	1.44E-03
	Methanol (kg)	2.09E-03
	CO_2(kg)	7.25E-03
	CO_2 from WWT (kg)	3.61E-02
	Ethylene carbonate (kg)	1.16E-03
Emissions to water	Ethylene oxide (kg)	5.74E-04
	Ethylene carbonate (kg)	1.14E-03
	Methanol (kg)	8.36E-04
	COD (kg)	3.20E-03
	BOD (kg)	3.20E-03
	TOC (kg)	1.09E-03
	DOC (kg)	1.09E-03
	Water (m^3)	3.61E-02

9. Production of EA

9.1. Fischer esterification

The production of ethyl acetate from acetic acid and ethanol is included in Ecoinvent. There is specific information for raw materials and energy, but the rest is generic.

9.2. Dehydrogenation of ethanol

Ethyl acetate can be produced by the dehydrogenation of ethanol using a copper/chromite/metallic copper/alumina/barium chromate catalyst [16]:

$$2C_2H_5OH \rightarrow C_4H_8O_2$$

We used the demonstration offered by Santacesaria *et al*[16] to compile the information presented in Table 24. In order to achieve higher conversion rates, a ratio of 0.005mol H_2/mol EtOH is kept.

Table 24 Efficiency of the production of EA through dehydrogenation and additional process information.

Process efficiency		
Reagent	*Ethanol*	
Conversion	64.83%	
Product	*EA*	*Acetic Aldehyde*
Selectivity	99.58%	0.42%
Molar yield	64.56%	0.27%
Yield (kg/kg)	0.62	0.003
Additional process information		
Emission to air	0.2%	
To WWTP	35.0%	

9.2.1. Infrastructure

As in 2.1.1

9.2.2. Raw materials and auxiliaries

We selected the Ecoinvent processes *market for ethanol, without water, in 99.7% solution state, from ethylene [GLO]* as the source for ethanol

9.2.3. Energy

No information was available on the energy consumption of the different stages. Thus, we proceeded as in 2.1.3.

9.2.4. Transportation

Since the reagent is available as market activity, no transport is required.

9.2.5. Emissions to air

See 2.1.5

9.2.6. Emissions to water

As per 2.1.6 and Table 24, 35% of the ethanol ends up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$\text{Ethanol: } 2C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

9.2.7. Life Cycle Inventory

The LCI of the production of 1 kg of EA is presented in Table 25.

Table 25 Life Cycle inventory of the production of 1kg of EA

	Inputs	
Infrastructure	Industrial plant (u)	4.03E-10
Raw materials and auxiliaries	H_2 (kg)	3.52E-04
	Ethanol (kg)	1.61E+00
	Water (m^3)	2.42E-02
Energy	Heat (MJ)	2.01E+00
	Electricity (kWh)	3.35E-01
	Outputs	
Products	EA	1.00E+00
	H_2 (kg)	2.23E-02
Emissions to air	Water (kg)	9.37E+00
	H_2(kg)	7.05E-07
	Ethanol (kg)	3.24E-03
	CO_2 from WWT (kg)	9.75E-01
Emissions to water	Ethanol (kg)	5.66E-02
	COD (kg)	1.18E-01
	BOD (kg)	1.18E-01
	TOC (kg)	2.96E-02
	DOC (kg)	2.96E-02
	Water (m^3)	1.48E-02

9.3. Avada process

The Avada process allows the synthesis of ethylene acetate from the reaction of ethene and acetic acid using a solid acid catalyst [17]:

$$CH_3COOH + CH_2CH_2$$

According to [17], butadiene is generated as byproduct. The conditions with minimized production and highest selectivity for EA are presented in Table 26, used to model the Avada process.

Table 26 Efficiency of the different stages for the production of EM through dehydrogenation and additional process information.

Process efficiency				
Reagent	*Ethene*		*Acetic acid*	
Conversion	42%		42%	
Product	*EA*	*Butene*	*EA*	*Butene*
Selectivity	99.85%	0.15%	99.9%	0.1%
Molar yield	42.00%	0.10%	42.00%	0.10%
Yield (kg/kg)	1.319	0.002	0.616	0.001
Additional process information				
Emission to air	0.2%		0.2%	

To WWTP	57.7%	57.7%

9.3.1. Infrastructure

As in 2.1.1

9.3.2. Raw materials and auxiliaries

We selected the Ecoinvent processes *market for ethylene, average [GLO]* and *market for acetic acid [RER]* for the two reagents required.

9.3.3. Energy

No information was available on the energy consumption at the different stages. Thus, we proceeded as in 2.1.3.

9.3.4. Transportation

Since all reagents are available as market activities, no transport is required.

9.3.5. Emissions to air

See 2.1.5

9.3.6. Emissions to water

As per 2.1.6 and Table 26, 57.7 % of the ethane and acetic acid end up in the WWTP, where they are removed with an efficiency of 90% according to the following reactions.

$$\text{Ethene: } C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$\text{Acetic Acid: } C_4H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

9.3.7. Life Cycle Inventory

The LCI for the production of 1 kg of EA is presented in Table 27 for the original process and in Table 28 for the optimized process.

Table 27 Life Cycle inventory of the production of 1kg of EA

	Inputs	
Infrastructure	Industrial plant (u)	4.01E-10
Raw materials and auxiliaries	Ethylene (kg)	7.58E-01
	Acetic acid (kg)	1.59E+00
	Water (m^3)	2.40E-02
Energy	Heat (MJ)	2.00E+00
	Electricity (kWh)	3.30E-01
	Outputs	
Products	EA (kg)	1.00E+00
Emissions to air	Water (kg)	9.31E+00
	Ethene (kg)	1.52E-03
	Acetic acid (kg)	3.25E-03
	CO_2 from WWT (kg)	2.47E+00
Emissions to water	Ethene (kg)	4.38E-02
	Acetic acid (kg)	9.37E-02
	COD (kg)	2.50E-01

	BOD (kg)	2.50E-01
	TOC (kg)	7.50E-02
	DOC (kg)	7.50E-02
	Water (m^3)	1.47E-02

Table 28 Life cycle inventory of the production of 1kg of EA (optimized)

	Inputs	
Infrastructure	Industrial plant (u)	4.00E-10
Raw materials and auxiliaries	Ethylene (kg)	3.36E-01
	Acetic acid (kg)	7.04E-01
	Water (m^3)	2.40E-02
Energy	Heat (MJ)	2.00E+00
	Electricity (kWh)	3.30E-01
	Outputs	
Products	EA (kg)	1.00E+00
Emissions to air	Water (kg)	9.31E+00
	Ethene (kg)	6.71E-04
	Acetic acid (kg)	1.44E-03
	CO_2 from WWT (kg)	9.11E-02
Emissions to water	Ethene (kg)	1.61E-03
	Acetic acid (kg)	3.45E-03
	COD (kg)	9.20E-03
	BOD (kg)	9.20E-03
	TOC (kg)	2.76E-03
	DOC (kg)	2.76E-03
	Water (m^3)	1.47E-02

9.4. Oxidation of butane

This process is included in Ecoinvent. There is specific information for raw materials and energy, the rest is generic.

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10. Data quality and sensitivity analysis

Data quality indicators for the different processes modeled are presented in Table 29. It is based on Table 0.1. found in [1], for which a summary is presented in Table 30. We used a slightly different meaning for items with a quality of “2”, partially based on literature, as opposed to based on a proxy process. However, the two most common quality values remain the same: “1” based on literature, and “3” estimated.

Table 29 Data quality indicators of the solvents under assessment

			Input materials	Water	Energy	Emissions
Car.	**DMC**	Shell Omega	1	1	1	3
	EC	from EO	*NA*	*NA*	*NA*	*NA*
Esters	**EA**	Fischer Esterification	*1*	*1*	*1*	*3*
		Dehydrogenation	1	3	3	3
		Avada	1	3	3	3
		Ox. of butane	*1*	*1*	*1*	*3*
	GBL	Reppe	*3*	*3*	*3*	*3*
		Hydro MAN	1	3	3	3
Ethers	**DME**	EO Cleavage	*3*	*3*	*3*	*3*
		DOW	3	3	3	3
		Shell Omega	1	3	3	3
		Hydration	*1*	*3*	*3*	*3*
	THF	Reppe	3	1	1	3
		Hydro. MAN	1	3	1	3
		Mitsubishi	2	3	3	3
Sulfones	**SL**	Hydro. Sulfolene	1	3	3	3
	EMS	MeSH+EtBr	2	3	2	3
		EtSH+CH_3Cl	3	3	3	3
		Average	1.71	2.53	2.35	3.00

Processes *in italics* are available in Ecoinvent. Based on : 1, literature; 2, literature (some stages) and estimations; 3 estimations

Table 30 Summary of data quality of the solvents described in [1]

	Input material	Water	Energy	Emissions	Solvents
Average	2.03	2.09	1.51	2.71	35.00

Based on: 1, literature; 2, proxy process; 3, estimated

Both we and Ecoinvent relied heavily on estimations such as the ones described in 2.1.5 and 2.1.6. for the emissions to water and air. To some extent, this is also the case for water use. The latter does not have an effect on the results presented in the paper, nor would affect other analysis based on the most common LCIA methods. It would however have tremendous importance if a Water Footprint is conducted. For this kind of studies, we do not suggest using the inventories here included.

While on average we were able to gather more data from literature than Ecoinvent in terms of material consumption, the opposite is true when it comes to energy use. To partially overcome this limitation, we conducted a sensitivity analysis based on the energy demand of the 22 solvent production processes described in [1] (Table 31) whose energy use is based on literature. We used the maximum and minimum demands of thermal and electrical energy as potential extremes for the energy demand of our processes.

Table 31 Energy demand of the 22 solvents in [1] with process specific data

Solvent	Steam (MJ)	Fuel (MJ)	Light fuel oil (kg)*	Thermal (MJ)	Electricity (kWh)
1	4.09			4.09	0.08
2	26.30			26.30	0.12
3	0.26	0.93		1.18	0.02
4	24.75			24.75	0.18
5	4.62			4.62	0.03
6	0.39			0.39	0.63
7	5.58			5.58	0.03
8	3.64			3.64	0.09
9	0.20			0.20	0.06
10	19.25			19.25	0.13
11	0.08			0.08	0.00
12	8.84			8.84	0.01
13	1.00			1.00	0.03
14	5.50			5.50	0.48
15	15.13			15.13	0.36
16	0.04			0.04	0.00
17			0.69	29.52	0.11
18	20.30		0.02	21.02	0.18
19	4.35			4.35	0.73
20	10.20		0.12	15.48	0.28
21	0.22			0.22	0.21
22	2.34			2.34	0.04
			Average	8.80	0.17
			Max	**29.52**	**0.73**
			Min	**0.037**	**0.0002**

* 1 kg= 42.6 MJ as described in [2]

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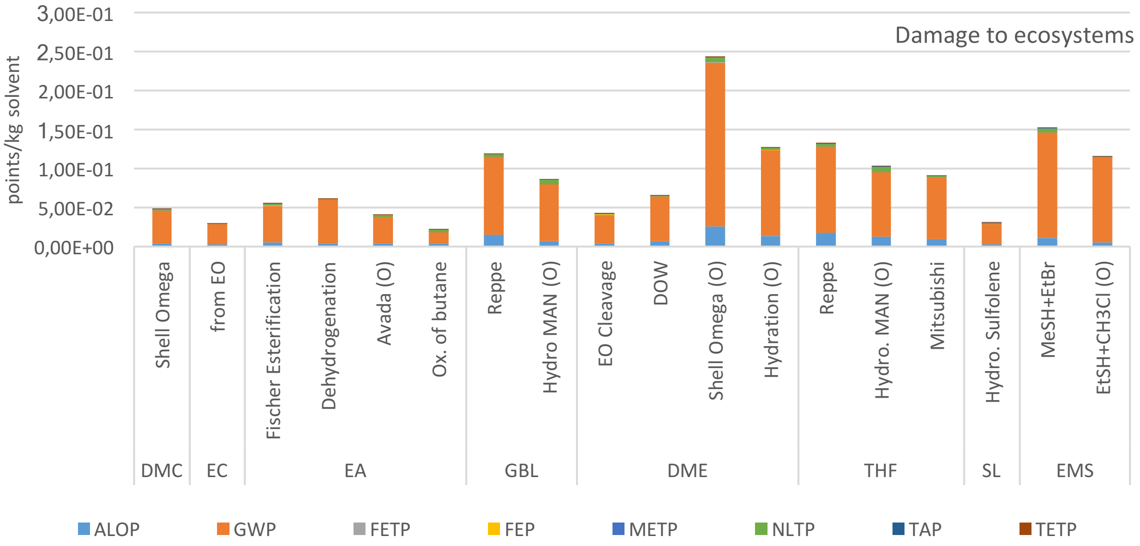
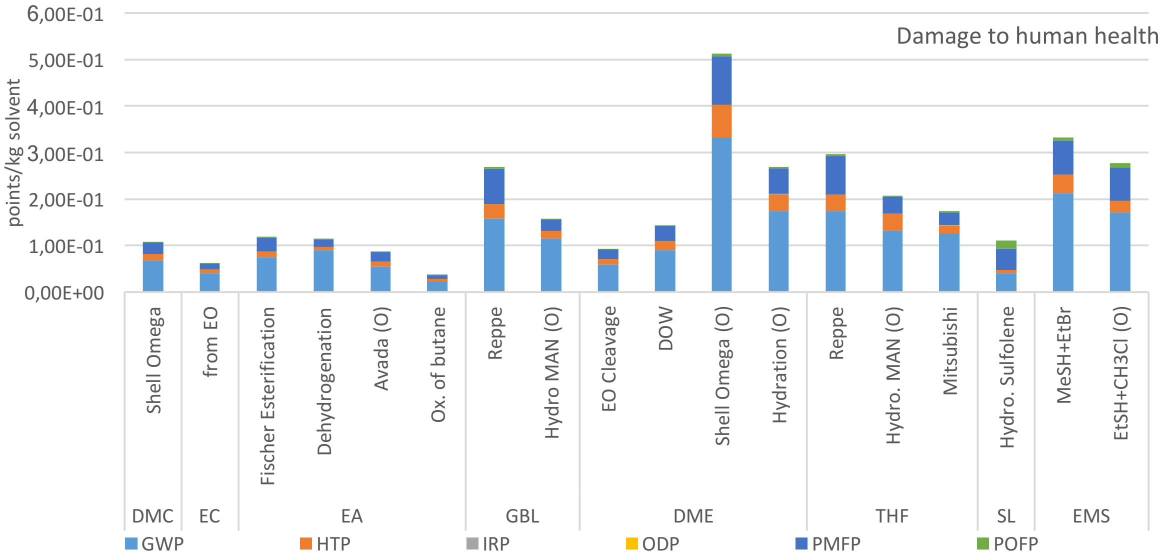
11. Additional LCIA results



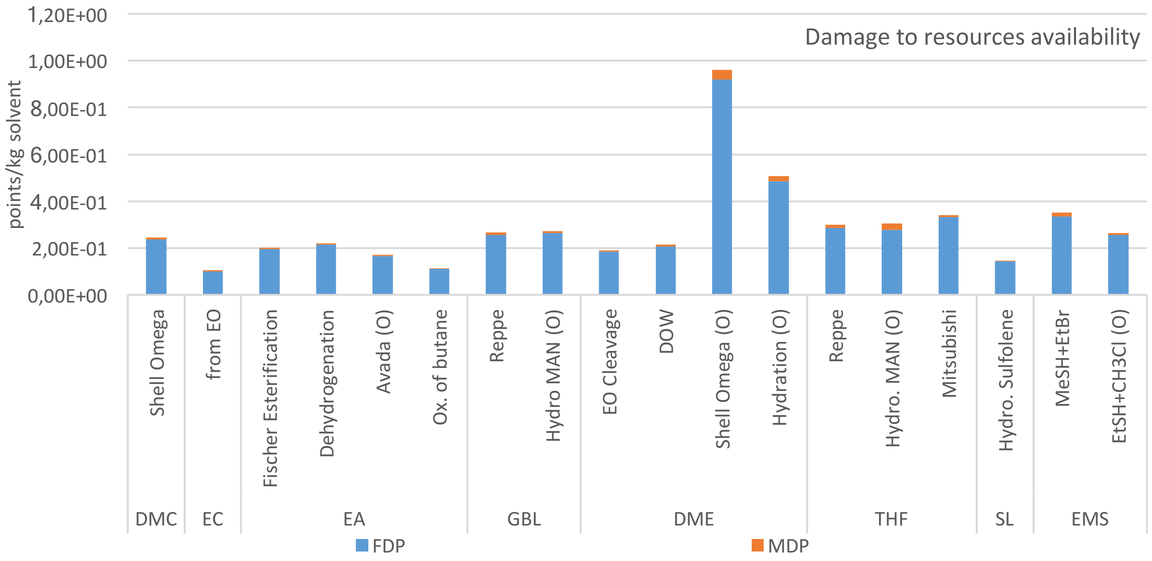
ALOP: agricultural land occupation, GWP: global warming, FETP: freshwater ecotoxicity, FEP: freshwater eutrophication, METP: marine ecotoxicity, NLTP: natural land transformation, TAP: terrestrial acidification potential, TETP: terrestrial ecotoxicity, ULOP: urban land occupation (O) Optimized process

Figure 4 Damages to ecosystems for the production of 1 kg of solvent



GWP: global warming, HTP: human toxicity, IRP: ionising radiation, ODP: ozone depletion, PMFP: particle matter formation, POFP: photochemical oxidant formation (O) Optimized process

Figure 5 Damages to human health for the production of 1 kg of solvent



FDP: fossil fuel depletion, and MDP: mineral resource depletion (O) Optimized process

Figure 6 Damages to resource availability for the production of 1 kg of solvent

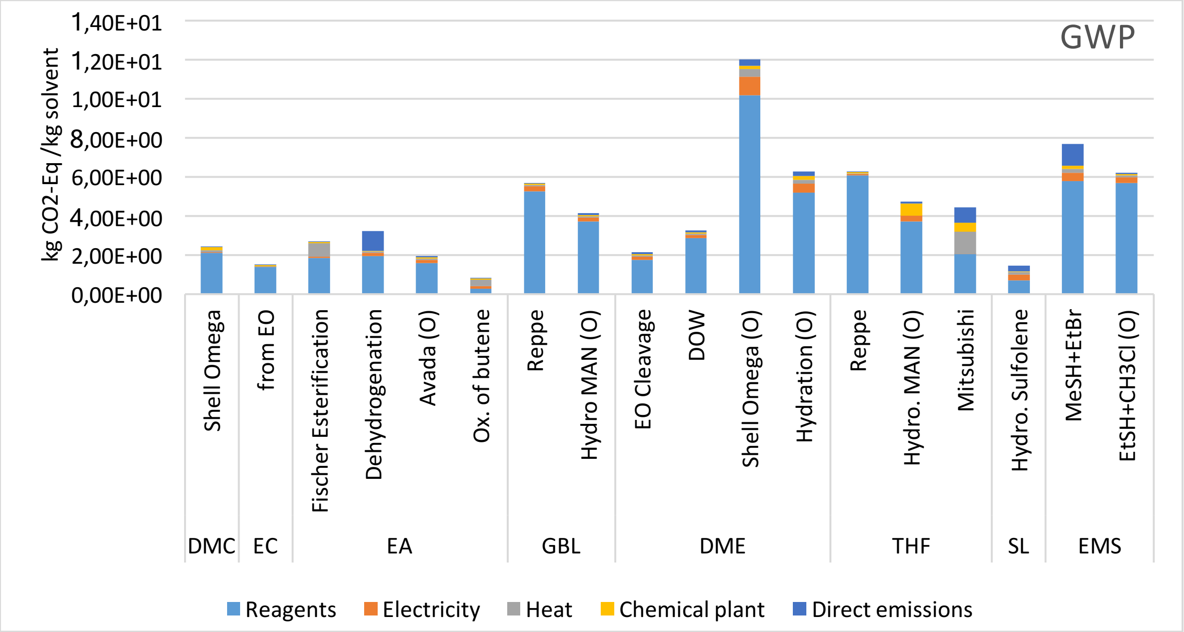


Figure 7 Sources of global warming potential for the production of 1 kg of solvent

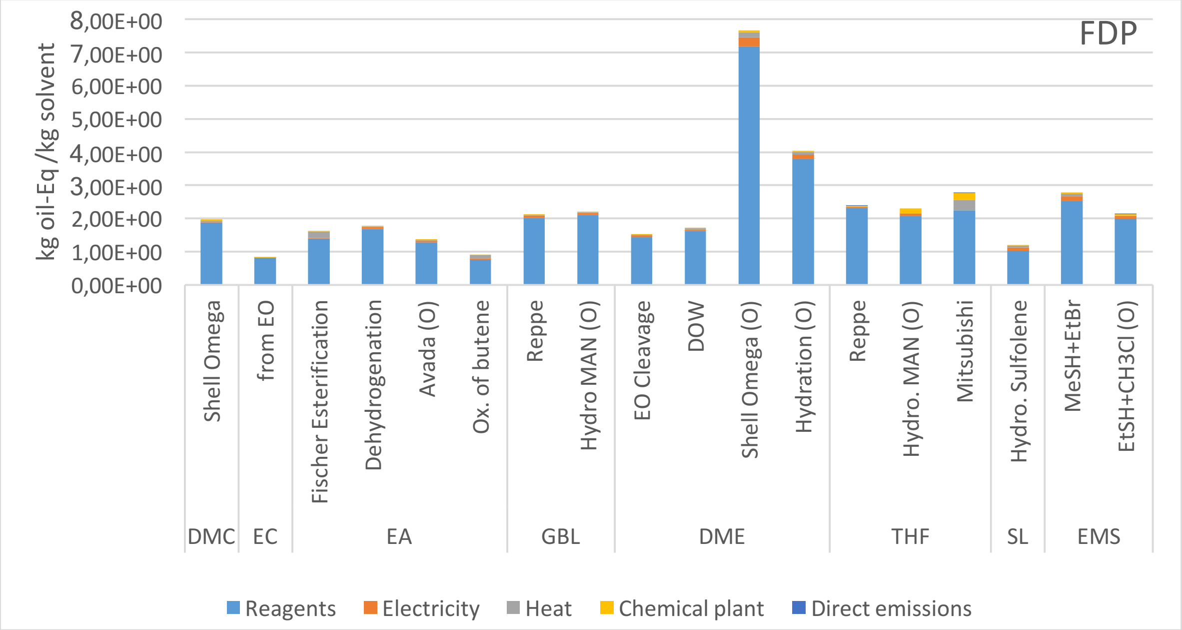


Figure 8 Sources of fossil fuel depletion potential for the production of 1 kg of solvent

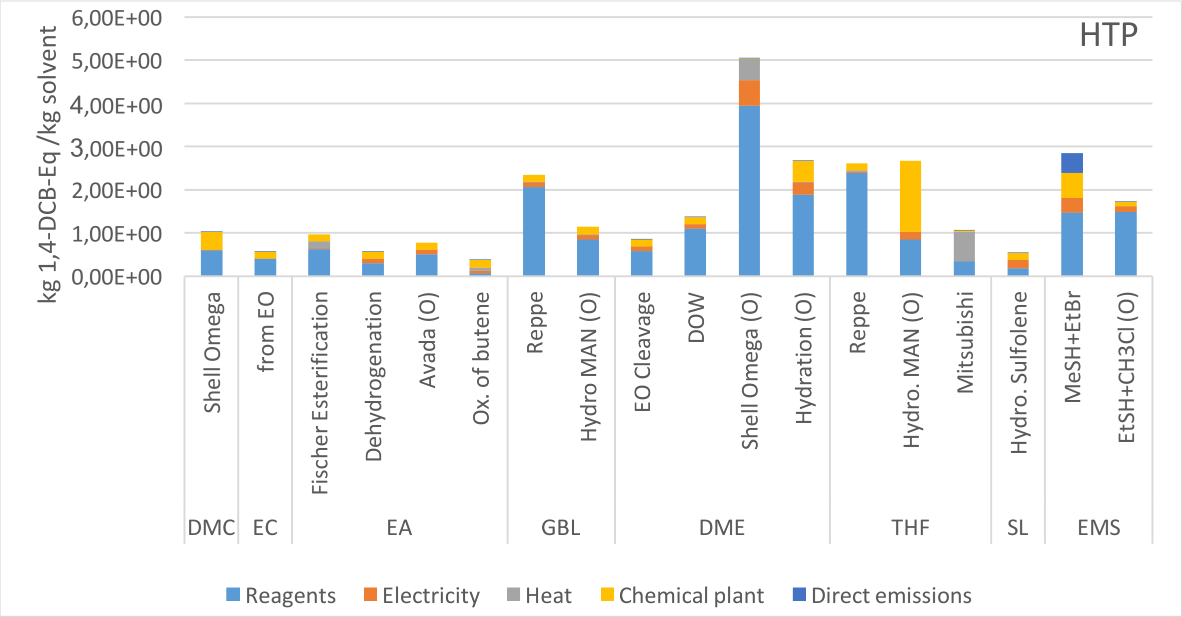


Figure 9 Sources of human toxicity potential for the production of 1 kg of solvent

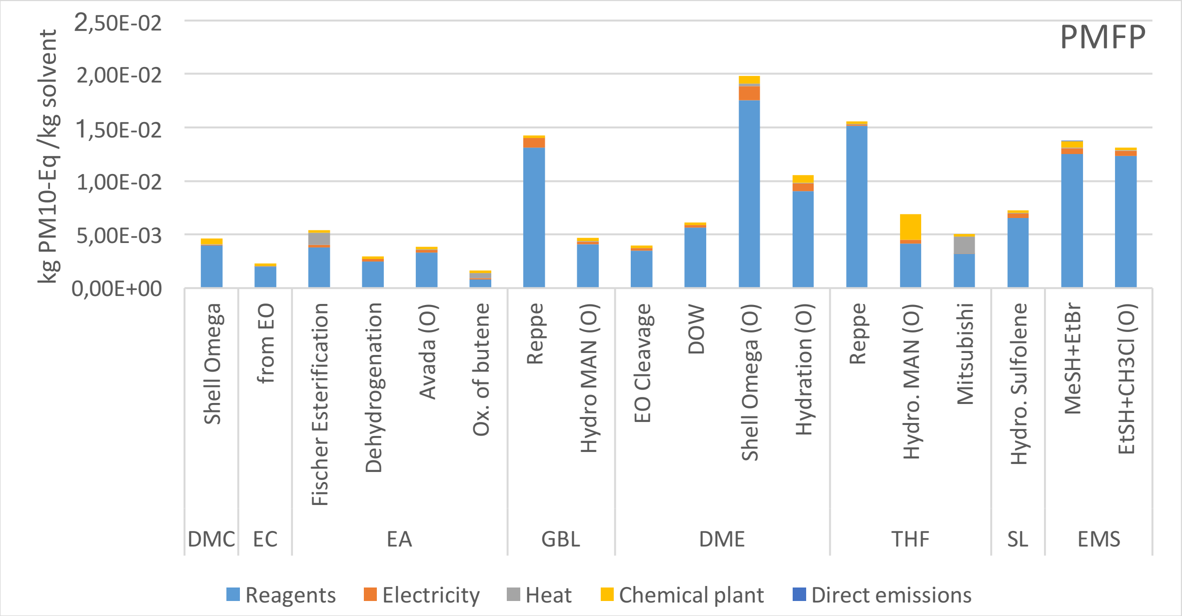


Figure 10 Sources of particulate matter formation potential for the production of 1 kg of solvents

agricultural land occupation	m2*a	9.36E-02	7.75E-02	1.48E-01	9.78E-02	1.76E-01	9.92E-0
climate change	kg CO2-Eq	2.45E+00	1.49E+00	2.69E+00	3.23E+00	6.35E+00	1.97E+0
fossil depletion	kg oil-Eq	1.97E+00	8.35E-01	1.62E+00	1.78E+00	2.99E+00	1.37E+0
freshwater ecotoxicity	kg 1,4-DCB-Eq	4.52E-02	2.42E-02	3.76E-02	2.40E-02	6.31E-02	3.26E-0
freshwater eutrophication	kg P-Eq	7.67E-04	4.92E-04	1.04E-03	1.02E-03	1.32E-03	7.13E-0
human toxicity	kg 1,4-DCB-Eq	1.04E+00	5.67E-01	9.67E-01	5.69E-01	1.43E+00	7.81E-0
ionising radiation	kg U235-Eq	1.81E-01	1.46E-01	2.17E-01	1.18E-01	4.98E-01	2.67E-0
marine ecotoxicity	kg 1,4-DCB-Eq	3.77E-02	2.25E-02	3.32E-02	2.24E-02	5.14E-02	2.87E-0
marine eutrophication	kg N-Eq	1.88E-03	1.10E-03	2.23E-03	1.73E-03	3.28E-03	1.59E-0
metal depletion	kg Fe-Eq	2.03E-01	1.11E-01	1.50E-01	1.16E-01	2.19E-01	1.27E-0
natural land transformation	m2	4.68E-04	1.05E-04	6.39E-04	1.41E-04	1.23E-03	5.74E-0
ozone depletion	kg CFC-11-Eq	2.48E-07	6.47E-08	3.18E-07	8.73E-08	6.30E-07	2.99E-0
particulate matter formation	kg PM10-Eq	4.64E-03	2.25E-03	5.41E-03	2.95E-03	7.99E-03	3.82E-0
photochemical oxidant formation	kg NMVOC	8.73E-03	4.22E-03	1.16E-02	1.28E-02	1.81E-02	8.39E-0
terrestrial acidification	kg SO2-Eq	1.18E-02	4.76E-03	1.32E-02	7.70E-03	1.83E-02	8.81E-0
terrestrial ecotoxicity	kg 1,4-DCB-Eq	1.86E-04	1.57E-04	3.92E-04	8.76E-05	7.89E-04	3.58E-0
urban land occupation	m2*a	1.72E-02	8.85E-03	2.03E-02	1.28E-02	2.73E-02	1.39E-0
water depletion	m3	6.24E-03	3.13E-03	7.07E-03	4.69E-03	1.14E-02	5.85E-0

Table 33 Midpoint impact categories for ethers and sulfones

		Ethers									
		DME						**THF**			
Impact category	**Reference unit**	**EO Cleavage**	**DOW**	**Shell Omega**	**Shell Omega (O)**	**Hydration**	**Hydration (O)**	**Reppe**	**Hydro. MAN**	**Hydro. MAN (O)**	**M**
agricultural land occupation	m2*a	9.25E-02	1.73E-01	6.42E-01	6.40E-01	4.04E-01	3.45E-01	4.90E-01	3.38E-01	3.22E-01	
climate change	kg CO2-Eq	2.14E+00	3.28E+00	1.34E+01	1.20E+01	8.76E+00	6.26E+00	6.28E+00	5.45E+00	4.74E+00	4
fossil depletion	kg oil-Eq	1.53E+00	1.71E+00	7.88E+00	7.66E+00	5.00E+00	4.05E+00	2.37E+00	2.56E+00	2.31E+00	2
freshwater ecotoxicity	kg 1,4-DCB-Eq	3.61E-02	5.36E-02	2.17E-01	2.14E-01	1.32E-01	1.13E-01	9.18E-02	1.21E-01	1.18E-01	
freshwater eutrophication	kg P-Eq	7.34E-04	1.40E-03	4.37E-03	4.33E-03	2.89E-03	2.45E-03	2.57E-03	2.19E-03	2.08E-03	
human toxicity	kg 1,4-DCB-Eq	8.56E-01	1.37E+00	5.11E+00	5.04E+00	3.14E+00	2.67E+00	2.61E+00	2.77E+00	2.67E+00	1
ionising radiation	kg U235-Eq	2.28E-01	3.80E-01	1.39E+00	1.39E+00	9.89E-01	8.40E-01	6.04E-01	8.76E-01	8.04E-01	
marine ecotoxicity	kg 1,4-DCB-Eq	3.03E-02	4.99E-02	1.87E-01	1.86E-01	1.17E-01	1.00E-01	8.20E-02	1.12E-01	1.09E-01	
marine eutrophication	kg N-Eq	1.66E-03	2.75E-03	9.08E-03	8.94E-03	5.76E-03	4.75E-03	5.54E-03	3.28E-03	3.04E-03	
metal depletion	kg Fe-Eq	1.43E-01	2.18E-01	9.11E-01	9.02E-01	5.33E-01	4.58E-01	2.92E-01	6.18E-01	6.05E-01	
natural land transformation	m2	3.82E-04	2.89E-04	1.90E-03	1.81E-03	9.34E-04	7.76E-04	9.53E-04	1.89E-03	1.71E-03	
ozone depletion	kg CFC-11-Eq	2.13E-07	6.07E-07	1.11E-06	1.06E-06	5.65E-07	4.74E-07	5.33E-07	1.02E-06	9.20E-07	
particulate matter formation	kg PM10-Eq	3.97E-03	6.14E-03	2.02E-02	1.98E-02	1.28E-02	1.06E-02	1.56E-02	7.40E-03	6.91E-03	

Ecosystems	Agricultural land occupation	points	3.67E-03	3.06E-03	5.53E-03	3.74E-03	6.94E-03	3.95
	Climate Change	points	4.28E-02	2.60E-02	4.72E-02	5.66E-02	1.11E-01	3.45
	Freshwater ecotoxicity	points	4.43E-05	1.99E-05	3.77E-05	1.96E-05	6.75E-05	3.17
	Freshwater eutrophication	points	7.72E-05	4.96E-05	1.05E-04	1.03E-04	1.33E-04	7.17
	Marine ecotoxicity	points	7.32E-06	4.14E-06	6.93E-06	4.12E-06	1.08E-05	5.83
	Natural land transformation	points	1.59E-03	3.70E-04	2.37E-03	4.76E-04	4.56E-03	2.10
	Terrestrial acidification	points	1.52E-04	6.10E-05	1.69E-04	9.87E-05	2.35E-04	1.13
	Terrestrial ecotoxicity	points	6.17E-05	5.19E-05	1.28E-04	2.83E-05	2.61E-04	1.19
	Urban land occupation	points	7.87E-04	4.06E-04	9.32E-04	5.86E-04	1.25E-03	6.35
	Subtotal	points	4.92E-02	3.01E-02	5.64E-02	6.17E-02	1.25E-01	4.15
Human Health	Climate change	points	6.78E-02	4.12E-02	7.46E-02	8.96E-02	1.76E-01	5.46
	Human toxicity	points	1.43E-02	7.80E-03	1.32E-02	7.78E-03	1.96E-02	1.07
	Ionising radiation	points	5.87E-05	4.75E-05	7.07E-05	3.85E-05	1.62E-04	8.69
	ozone depletion	points	1.23E-05	2.86E-06	1.61E-05	4.16E-06	3.19E-05	1.50
	Particulate matter formation	points	2.44E-02	1.20E-02	2.90E-02	1.61E-02	4.22E-02	2.01
	Photochemical oxidant formation	points	1.14E-03	8.23E-04	2.79E-03	2.13E-03	2.49E-03	1.14
	Subtotal	points	1.08E-01	6.18E-02	1.20E-01	1.16E-01	2.41E-01	8.67
Resources	Fossil depletion	points	2.37E-01	1.00E-01	1.95E-01	2.14E-01	3.58E-01	1.65
	Metal depletion	points	9.41E-03	5.14E-03	6.95E-03	5.40E-03	1.01E-02	5.89
	Subtotal	points	2.46E-01	1.05E-01	2.02E-01	2.19E-01	3.68E-01	1.70
	Total	points	4.03E-01	1.97E-01	3.78E-01	3.96E-01	7.33E-01	2.99

Ecosystems	Agricultural land occupation	points	3.75E-03	6.90E-03	2.58E-02	2.58E-02	1.65E-02	1.41E-02	1.83E-02	1.34E-02	1.28E-02
	Climate Change	points	3.75E-02	5.74E-02	2.34E-01	2.10E-01	1.54E-01	1.10E-01	1.10E-01	9.56E-02	8.31E-02
	Freshwater ecotoxicity	points	3.73E-05	4.76E-05	2.09E-04	2.04E-04	1.25E-04	1.05E-04	1.04E-04	9.48E-05	9.07E-05
	Freshwater eutrophication	points	7.39E-05	1.41E-04	4.40E-04	4.36E-04	2.91E-04	2.47E-04	2.58E-04	2.20E-04	2.09E-04
	Marine ecotoxicity	points	6.26E-06	9.84E-06	3.71E-05	3.67E-05	2.33E-05	1.98E-05	1.93E-05	1.98E-05	1.90E-05
	Natural land transformation	points	1.29E-03	1.04E-03	6.33E-03	6.04E-03	3.18E-03	2.63E-03	3.34E-03	7.19E-03	6.51E-03
	Terrestrial acidification	points	1.27E-04	1.56E-04	6.58E-04	6.38E-04	3.93E-04	3.24E-04	4.23E-04	2.25E-04	2.09E-04
	Terrestrial ecotoxicity	points	5.33E-05	1.18E-04	4.45E-04	4.35E-04	1.47E-04	1.22E-04	1.63E-04	1.07E-04	1.01E-04
	Urban land occupation	points	6.88E-04	1.16E-03	3.61E-03	3.55E-03	2.18E-03	1.83E-03	2.26E-03	2.21E-03	2.09E-03
	Subtotal	points	4.35E-02	6.70E-02	2.72E-01	2.48E-01	1.76E-01	1.29E-01	1.35E-01	1.19E-01	1.05E-01
Human Health	Climate change	points	5.93E-02	9.09E-02	3.70E-01	3.33E-01	2.43E-01	1.74E-01	1.74E-01	1.51E-01	1.31E-01
	Human toxicity	points	1.18E-02	1.88E-02	7.04E-02	6.94E-02	4.33E-02	3.68E-02	3.55E-02	3.82E-02	3.68E-02
	Ionising radiation	points	7.41E-05	1.24E-04	4.54E-04	4.51E-04	3.22E-04	2.73E-04	1.97E-04	2.85E-04	2.62E-04
	ozone depletion	points	1.04E-05	3.63E-05	5.36E-05	5.13E-05	2.65E-05	2.22E-05	2.64E-05	5.14E-05	4.64E-05
	Particulate matter formation	points	2.08E-02	3.24E-02	1.06E-01	1.04E-01	6.76E-02	5.56E-02	8.24E-02	3.90E-02	3.63E-02
	Photochemical oxidant formation	points	8.72E-04	1.78E-03	5.10E-03	5.09E-03	3.65E-03	2.95E-03	5.09E-03	1.97E-03	1.80E-03
	Subtotal	points	9.28E-02	1.44E-01	5.53E-01	5.12E-01	3.58E-01	2.69E-01	2.97E-01	2.31E-01	2.07E-01
Resources	Fossil depletion	points	1.83E-01	2.06E-01	9.45E-01	9.19E-01	5.99E-01	4.85E-01	2.85E-01	3.07E-01	2.77E-01
	Metal depletion	points	6.62E-03	1.01E-02	4.23E-02	4.18E-02	2.47E-02	2.12E-02	1.35E-02	2.86E-02	2.80E-02
	Subtotal	points	1.90E-01	2.16E-01	9.87E-01	9.61E-01	6.24E-01	5.07E-01	2.98E-01	3.35E-01	3.05E-01
	Total	points	3.26E-01	4.27E-01	1.81E+00	1.72E+00	1.16E+00	9.05E-01	7.30E-01	6.85E-01	6.17E-01

Table 36 Global warming potential (kg CO2 Eq./kg solvent)

			Reagents	Electricity	Heat	Chemical plant	Direct emissions
Carbonates	**DMC**	**Shell Omega**	2.12E+00	2.76E-02	9.90E-02	1.53E-01	4.35E-02
	EC	**from EO**	1.41E+00	1.49E-03	4.90E-03	6.24E-02	5.35E-03
Esters	**EA**	**Fischer Esterification**	1.85E+00	5.98E-02	7.12E-01	6.25E-02	8.08E-03
		Dehydrogenation	1.94E+00	1.60E-01	6.59E-02	6.27E-02	1.00E+00
		Avada	3.59E+00	1.59E-01	6.54E-02	6.28E-02	2.47E+00
		Avada (O)	1.59E+00	1.58E-01	6.56E-02	6.26E-02	9.11E-02
		Ox. of butene	2.99E-01	1.03E-01	3.45E-01	6.35E-02	9.59E-03
	GBL	**Reppe**	5.27E+00	2.67E-01	7.05E-02	6.20E-02	2.16E-02
		Hydro MAN	5.13E+00	1.78E-01	7.40E-02	7.01E-02	7.52E+00
		Hydro MAN (O)	3.73E+00	1.78E-01	7.36E-02	7.03E-02	1.07E-01
Ethers	**DME**	**EO Cleavage**	1.76E+00	1.57E-01	6.56E-02	6.24E-02	9.23E-02
		DOW	2.88E+00	1.57E-01	6.55E-02	6.23E-02	1.10E-01
		Shell Omega	1.03E+01	9.47E-01	3.90E-01	1.86E-01	1.51E+00
		Shell Omega (O)	1.02E+01	9.46E-01	3.90E-01	1.86E-01	3.21E-01
		Hydration	6.49E+00	4.73E-01	1.95E-01	1.86E-01	1.42E+00
		Hydration (O)	5.18E+00	4.73E-01	1.95E-01	1.85E-01	2.25E-01
	THF	**Reppe**	6.09E+00	5.27E-02	5.27E-02	6.21E-02	1.88E-02
		Hydro. MAN	4.17E+00	2.81E-01	5.45E-04	6.24E-01	3.76E-01
		Hydro. MAN (O)	3.73E+00	2.81E-01	4.74E-04	6.24E-01	1.11E-01
		Mitsubishi	2.06E+00	4.53E-04	1.13E+00	4.66E-01	8.00E-01
Sulfones	**SL**	**Hydro. Sulfolene**	6.97E-01	3.17E-01	1.31E-01	3.63E-02	2.80E-01
	EMS	**MeSH+BrEt**	5.79E+00	4.39E-01	1.82E-01	1.73E-01	1.11E+00
		EtSH+CH3Cl	5.14E+00	4.35E-01	1.80E-01	1.71E-01	9.50E-01
		EtSH+CH3Cl (O)	5.69E+00	2.81E-01	1.15E-01	5.03E-02	6.95E-02

Table 37 Fossil depletion potential (kg oil Eq./kg solvent)

			Reagents	Electricity	Heat	Chemical plant	Direct emissions
Carbonates	**DMC**	**Shell Omega**	1.89E+00	7.90E-03	4.18E-02	3.85E-02	0.00E+00
	EC	**from EO**	8.17E-01	4.18E-04	2.01E-03	1.57E-02	0.00E+00
Esters	**EA**	**Fischer Esterification**	1.40E+00	1.57E-02	1.91E-01	1.57E-02	0.00E+00
		Dehydrogenation	1.69E+00	4.56E-02	2.78E-02	1.59E-02	-1.78E-04
		Avada	2.90E+00	4.51E-02	2.78E-02	1.58E-02	-2.99E-04
		Avada (O)	1.28E+00	4.50E-02	2.77E-02	1.58E-02	-1.37E-04
		Ox. of butene	7.62E-01	2.93E-02	1.13E-01	1.60E-02	-9.20E-05
	GBL	**Reppe**	2.01E+00	7.02E-02	2.85E-02	1.55E-02	0.00E+00
		Hydro MAN	2.91E+00	5.08E-02	3.12E-02	1.77E-02	-3.00E-04
		Hydro MAN (O)	2.11E+00	5.06E-02	3.12E-02	1.77E-02	0.00E+00
Ethers	**DME**	**EO Cleavage**	1.44E+00	4.47E-02	2.77E-02	1.58E-02	-1.53E-04
		DOW	1.63E+00	4.46E-02	2.76E-02	1.58E-02	0.00E+00
		Shell Omega	7.40E+00	2.69E-01	1.65E-01	4.65E-02	0.00E+00
		Shell Omega (O)	7.18E+00	2.69E-01	1.65E-01	4.67E-02	-7.66E-04
		Hydration	4.73E+00	1.34E-01	8.24E-02	4.65E-02	0.00E+00
		Hydration (O)	3.78E+00	1.34E-01	8.26E-02	4.65E-02	0.00E+00
	THF	**Reppe**	2.33E+00	1.50E-02	1.38E-02	1.57E-02	2.37E-04
		Hydro. MAN	2.32E+00	7.98E-02	0.00E+00	1.57E-01	0.00E+00
		Hydro. MAN (O)	2.07E+00	7.99E-02	2.31E-04	1.57E-01	0.00E+00
		Mitsubishi	2.24E+00	0.00E+00	3.21E-01	1.96E-01	2.78E-04
Sulfones	**SL**	**Hydro. Sulfolene**	1.03E+00	9.02E-02	5.53E-02	1.56E-02	0.00E+00
	EMS	**MeSH+BrEt**	2.53E+00	1.29E-01	7.88E-02	4.48E-02	0.00E+00
		EtSH+CH3Cl	2.17E+00	1.26E-01	7.76E-02	4.42E-02	0.00E+00
		EtSH+CH3Cl (O)	2.00E+00	7.59E-02	1.19E-02	4.63E-02	2.13E-04

Table 38 Particle matter formation potential (kg PM10 Eq./kg solvent)

			Reagents	Electricity	Heat	Chemical plant	Direct emissions
Carbonates	**DMC**	**Shell Omega**	3.96E-03	3.94E-05	4.92E-05	5.90E-04	0.00E+00
	EC	**from EO**	2.00E-03	4.96E-06	3.38E-06	2.40E-04	0.00E+00
Esters	**EA**	**Fischer Esterification**	3.81E-03	1.95E-04	1.17E-03	2.40E-04	0.00E+00
		Dehydrogenation	2.44E-03	2.29E-04	3.27E-05	2.42E-04	0.00E+00
		Avada	7.49E-03	2.26E-04	3.28E-05	2.41E-04	7.99E-07
		Avada (O)	3.32E-03	2.26E-04	3.24E-05	2.41E-04	0.00E+00
		Ox. of butene	7.72E-04	1.47E-04	4.38E-04	2.45E-04	-1.60E-07
	GBL	**Reppe**	1.31E-02	8.71E-04	4.86E-05	2.38E-04	0.00E+00
		Hydro MAN	5.63E-03	2.54E-04	3.65E-05	2.70E-04	0.00E+00
		Hydro MAN (O)	4.09E-03	2.54E-04	3.67E-05	2.71E-04	-4.65E-07
Ethers	**DME**	**EO Cleavage**	3.47E-03	2.24E-04	3.25E-05	2.40E-04	0.00E+00
		DOW	5.64E-03	2.24E-04	3.25E-05	2.40E-04	0.00E+00
		Shell Omega	1.80E-02	1.35E-03	1.94E-04	7.14E-04	0.00E+00
		Shell Omega (O)	1.75E-02	1.35E-03	1.94E-04	7.15E-04	0.00E+00
		Hydration	1.13E-02	6.75E-04	9.75E-05	7.15E-04	0.00E+00
		Hydration (O)	9.07E-03	6.75E-04	9.71E-05	7.15E-04	-1.06E-06
	THF	**Reppe**	1.52E-02	7.64E-05	9.66E-05	2.40E-04	0.00E+00
		Hydro. MAN	4.60E-03	4.01E-04	0.00E+00	2.40E-03	7.40E-07
		Hydro. MAN (O)	4.11E-03	4.02E-04	0.00E+00	2.40E-03	0.00E+00
		Mitsubishi	3.17E-03	1.60E-06	1.61E-03	2.32E-04	-5.32E-07
Sulfones	**SL**	**Hydro. Sulfolene**	6.50E-03	4.52E-04	6.53E-05	2.40E-04	0.00E+00
	EMS	**MeSH+BrEt**	1.25E-02	5.37E-04	7.67E-05	5.70E-04	1.37E-06
		EtSH+CH3Cl	1.30E-02	6.13E-04	8.87E-05	6.50E-04	-1.43E-06
		EtSH+CH3Cl (O)	1.23E-02	4.77E-04	6.81E-05	2.29E-04	-1.31E-06

Table 39 Human toxicity potential (kg 1,4-DCB-Eq/kg solvent)

			Reagents	Electricity	Heat	Chemical plant	Direct emissions
Carbonates	**DMC**	**Shell Omega**	5.95E-01	1.70E-02	4.97E-03	4.03E-01	1.62E-02
	EC	**from EO**	3.99E-01	6.24E-04	2.83E-04	1.64E-01	2.55E-03
Esters	**EA**	**Fischer Esterification**	6.23E-01	2.38E-02	1.56E-01	1.64E-01	0.00E+00
		Dehydrogenation	3.02E-01	9.86E-02	3.30E-03	1.65E-01	5.69E-05
		Avada	1.16E+00	9.75E-02	3.29E-03	1.64E-01	1.43E-04
		Avada (O)	5.15E-01	9.74E-02	3.28E-03	1.65E-01	0.00E+00
		Ox. of butene	5.94E-02	6.33E-02	8.25E-02	1.67E-01	3.72E-05
	GBL	**Reppe**	2.07E+00	1.06E-01	4.45E-03	1.63E-01	-2.34E-04
		Hydro MAN	1.17E+00	1.10E-01	3.67E-03	1.85E-01	0.00E+00
		Hydro MAN (O)	8.50E-01	1.10E-01	3.67E-03	1.85E-01	0.00E+00
Ethers	**DME**	**EO Cleavage**	5.87E-01	9.65E-02	3.25E-03	1.64E-01	5.31E-03
		DOW	1.11E+00	9.65E-02	3.29E-03	1.64E-01	1.37E-04
		Shell Omega	4.02E+00	5.81E-01	1.94E-02	4.88E-01	2.04E-03
		Shell Omega (O)	3.95E+00	5.81E-01	4.88E-01	1.97E-02	1.51E-03
		Hydration	2.36E+00	2.91E-01	9.75E-03	4.88E-01	9.43E-04
		Hydration (O)	1.88E+00	2.90E-01	9.88E-03	4.88E-01	8.01E-04
	THF	**Reppe**	2.39E+00	3.26E-02	2.01E-02	1.64E-01	0.00E+00
		Hydro. MAN	9.55E-01	1.73E-01	0.00E+00	1.64E+00	0.00E+00
		Hydro. MAN (O)	8.53E-01	1.73E-01	0.00E+00	1.64E+00	0.00E+00
		Mitsubishi	3.39E-01	2.56E-04	6.94E-01	2.34E-02	1.11E-02
Sulfones	**SL**	**Hydro. Sulfolene**	1.79E-01	1.95E-01	6.59E-03	1.64E-01	4.89E-03
	EMS	**MeSH+BrEt**	1.47E+00	3.42E-01	1.14E-02	5.76E-01	4.58E-01
		EtSH+CH3Cl	8.67E-01	2.82E-01	9.46E-03	4.76E-01	3.78E-01
		EtSH+CH3Cl (O)	1.49E+00	1.29E-01	4.30E-03	9.89E-02	3.44E-04