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ELECTRONIC SUPPORTING INFORMATION
Role of Life Cycle Externalities in the Valuation of Protic Ionic Liquids – A Case Study in Biomass Pretreatment Solvents

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Appendix A. Modeling and simulation

This section details the properties used for the pseudo components in Aspen-HYSYS v9 for process simulation. For estimating the enthalpy of formation, the molecular structure of the cation and anion are first drawn and optimized in a molecular modeling and graphics software such as ArgusLab. The structure is then processed with the quantum chemistry tool MOPAC, an open source software applied here for calculating the charge density profiles and enthalpies of formation. The heat of formation of ionic liquids (ILs) is obtained as shown in Equation S1 below from the Born-Haber cycle[4].

$$\Delta H^{\circ}_{f_{\mathrm{IL}}} = \Delta H^{\circ}_{\mathrm{f_{cation}}} + \Delta H^{\circ}_{\mathrm{f_{anion}}} - \Delta H_{\mathrm{L}} \tag{S1}$$

ΔH_{L} is the lattice energy calculated from Equation S2 below[6].

$$\Delta H_{\mathrm{L}} = U_{\mathrm{pot}} + \left[p\left(\frac{n_{\mathrm{m}}}{2} - 2\right) + q\left(\frac{n_{\mathrm{x}}}{2} - 2\right)\right] RT \tag{S2}$$

The parameters n_{m} and n_{x} depend on the nature of the cation and anion, respectively. They are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for non-linear polyatomic ions. p and q are the oxidation states of the cation and anion, respectively. The potential energy U_{pot} is calculated from Equation S3 below.

$$U_{\mathrm{pot}} = \gamma \left(\frac{\rho_{\mathrm{m}}}{M_{\mathrm{m}}}\right)^{1/3} + \delta \tag{S3}$$

The parameters ρ_{m} and M_{m} denote the density and the molecular weight of the IL, respectively. The coefficients γ and δ depend on the stoichiometry of the IL.

Table S1: 1-methylimidazole properties

Property	**Value**	**Units**
MW	82.10	g mol^{-1}
BP	198 [1]	°C
Density	1030 [1]	kg m^{-3}
ΔH_f	125700 [10]	kJ kmol^{-1}
T_c	490.90	°C
P_c	6086	kPa
V_c	0.26	m^3 kmol^{-1}
Acentricity	0.35	–

Table S2: [HMIM][HSO_4] properties

Property	**Value**	**Units**
MW	180.20	g mol^{-1}
BP	401.800 [9]	°C
Density	1484 [9]	kg m^{-3}
ΔH_f	-938000	kJ kmol^{-1}
T_c	739.6 [9]	°C
P_c	9189 [9]	kPa
V_c	0.43 [9]	m^3 kmol^{-1}
Acentricity	0.67 [9]	–

Table S3: [TEA][HSO_4] properties

Property	**Value**	**Units**
MW	199.30	g mol^{-1}
BP	377.10 [9]	°C
Density	1143 [9]	kg/m^3
ΔH_f	-884100	kJ kmol^{-1}
T_c	644.30 [9]	°C
P_c	4732 [9]	kPa
V_c	0.62 [9]	m^3 kmol^{-1}
Acentricity	0.74 [9]	–

Appendix B. Economic assessment

This appendix details the breakdown of the capital and operational expenditures, the prices of raw materials, and the costing results obtained from process simulation. The CAPEX consists of equipment costs, offsite costs, engineering and construction costs, and contingency charges. The equipment costs were estimated using Equation S4 below[8].

$$C_{\mathrm{ISBL}} = \sum_{e \in \mathrm{Equipment}} F_e C_e \tag{S4}$$

Here, C_e is the cost of purchased equipment e on a U.S. Gulf Coast basis as of January 2006, and F_e is the corresponding equipment installation factor. Due to unavailability of current equipment data, their costs are calculated as:

$$C_e = a + bS^n \tag{S5}$$

where a and b are cost constants, n is equipment type exponent and S is a size parameter. Finally, because of inflation, capital costs need to be escalated to reflect up-to-date costs. This is usually done using cost indices:

$$\mathrm{Cost}_{\mathrm{new}} = \mathrm{Cost}_{\mathrm{old}} + \frac{\text{Cost index}_{\mathrm{new}}}{\text{Cost index}_{\mathrm{old}}} \tag{S6}$$

In this work, the Chemical Engineering Plant Cost Index (CEPCI) for 2006 and 2019 are used. CEPCI is one of the most commonly-used published composite indices and was developed based on 4 main components: process equipment, construction labor, buildings and supervision and engineering.

Table S4: Breakdown of cost estimation

CAPEX, C_{CAPEX}
Fixed capital, C_{FC}:
Onsite capital costs, ISBL
Equipment cost
Offsite capital costs, OSBL = 40% ISBL
Engineering and construction costs, $C_{\text{Eng}} = 10\%(\text{ISBL} + \text{OSBL})$
Contingency charges, $C_{\text{Con}} = 15\%$ (ISBL + OSBL)
OPEX, C_{OPEX}
Variable cost of production, C_{VCP}:
Raw materials, C_{RM}
Utilities, C_{U}
Fixed cost of production, C_{FCP}:
Operation labor, $C_{\text{OL}} = 720,000\text{USD}_{2019}$[1]
Supervision, $C_{Sup} = 25\% C_{\text{OL}} = 180,000\text{USD}_{2019}$
Salaries, $C_{\text{Sal}} = 50\%(C_{\text{OL}} + C_{\text{Sup}}) = 450,000\text{USD}_{2019}$
Maintenance, $C_{\text{Main}} = 3\%\text{ISBL}$
Land, $C_{\text{Land}} = 1\%(\text{ISBL} + \text{OSBL})$
Taxes and insurance, $C_{\text{Tax}} = 1.5\% C_{\text{FC}}$
General plant overhead, $C_{\text{GPO}} = 65\%(C_{\text{OL}} + C_{\text{Sup}} + C_{\text{Sal}} + C_{\text{Main}})$

[a] Based on 4.8 operator per shift with 3 shift positions and an average salary of $50k per operator.

Table S5: Commodity prices used in economic assessment

Commodity	**Price ($)**
Methylamine (kg)	0.98
Glyoxal (kg)	1.78
Formaldehyde (kg)	0.38
Ammonia (kg)	0.56
Sulfuric acid (kg)	0.05
Triethylamine (kg)	1.36
Ionized water (m^3)	0.87
Cooling water (kg)	0.50
Steam (1000 kg)	25.0
Electricity (kWh)	0.16

Table S6: Detailed CAPEX costs for 1-methylimidazole

Unit	**Specifications**		**Eq. Cost ($ kg^{-1})**
Flash Tank	Diameter / Length (m)	6.35 / 22.22	1.48×10^{-4}
Reactor	Volume (m^3)	13.59	2.17×10^{-4}
Heater	Area (m^2)	2160.68	7.15×10^{-4}
Cooler 1	Area (m^2)	159.45	7.15×10^{-4}
Cooler 2	Area (m^2)	2265.48	7.15×10^{-4}
Cooling Tower	Vol Flow (L s^{-1})	4624.28	1.67×10^{-3}
Pump 1	Vol Flow (L s^{-1})	5.49	7.25×10^{-6}
Pump 2	Vol Flow (L s^{-1})	13.81	8.74×10^{-6}
Pump 3	Vol Flow (L s^{-1})	1.96	6.73×10^{-6}
Compressor 1	Power (kWh)	497.51	1.69×10^{-4}
Compressor 2	Power (kWh)	520.19	1.74×10^{-4}
Compressor 3	Power (kWh)	519.87	1.74×10^{-4}
Compressor 4	Power (kWh)	7621.36	8.28×10^{-4}
CAPEX Component			**Total Cost ($ kg^{-1})**
ISBL			4.1×10^{-3}
OSBL			1.6×10^{-3}
C_{Eng}			5.8×10^{-4}
C_{Con}			8.6×10^{-4}

Table S7: Detailed OPEX costs for 1-methylimidazole

Feedstock/Utility	**Cost ($ kg^{-1})**
Methylamine	0.39
Glyoxal	1.34
Formaldehyde	0.15
Ammonia	0.12
Water	2×10^{-4}
Steam	0.03
Cooling Water	0.73
Electricity	0.05
OPEX Component	**Total Cost ($ kg^{-1})**
C_{CVP}	2.8235
C_{FCP}	0.0130

Table S8: Detailed CAPEX costs for [HMIM][HSO_4]

Unit	Specifications		Eq. Cost ($ kg^{-1})
Flash Tank	Diameter / Length (m)	3.55 / 12.80	1.48×10^{-4}
Reactor	Volume (m^3)	4.19	1.11×10^{-4}
Heater	Area (m^2)	227.21	8.74×10^{-4}
Cooler 1	Area (m^2)	299.69	8.74×10^{-4}
Cooler 2	Area (m^2)	136.58	8.74×10^{-4}
Cooler 3	Area (m^2)	4969.67	8.74×10^{-4}
Cooling Tower	Vol Flow (L s^{-1})	1211.98	5.54×10^{-4}
Pump 1	Vol Flow (L s^{-1})	2.45	6.80×10^{-6}
Pump 2	Vol Flow (L s^{-1})	12.16	8.42×10^{-6}
Pump 3	Vol Flow (L s^{-1})	2.30	6.78×10^{-6}
Pump 4	Vol Flow (L s^{-1})	10.07	8.04×10^{-6}
Pump 5	Vol Flow (L s^{-1})	2.08	6.75×10^{-6}
Pump 6	Vol Flow (L s^{-1})	3.69	6.98×10^{-6}
CAPEX Component			**Total Cost ($ kg^{-1})**
ISBL			1.68×10^{-3}
OSBL			6.72×10^{-4}
C_{Eng}			2.35×10^{-4}
C_{Con}			3.53×10^{-4}

Table S9: Detailed OPEX costs for [HMIM][HSO_4]

Feedstock/Utility	Cost ($ kg^{-1})
Sulfuric Acid	0.03
1-Methylimidazole	1.30
Water	2×10^{-4}
Steam	4×10^{-3}
Cooling Water	0.12
Electricity	1.37×10^{-5}
OPEX Component	**Total Cost ($ kg^{-1})**
C_{CVP}	1.45
C_{FCP}	0.0108

Table S10: Detailed CAPEX costs for [TEA][HSO_4]

Unit	**Specifications**		**Eq. Cost ($ kg^{-1})**
Flash Tank	Diameter / Length (m)	3.21 / 11.30	9.08×10^{-5}
Reactor	Volume (m^3)	3.79	1.05×10^{-4}
Heater	Area (m^2)	191.93	3.36×10^{-4}
Cooler 1	Area (m^2)	244.19	3.36×10^{-4}
Cooler 2	Area (m^2)	133.09	3.36×10^{-4}
Cooler 3	Area (m^2)	1527.61	3.36×10^{-4}
Cooling Tower	Vol Flow (L s^{-1})	575.07	3.20×10^{-4}
Pump 1	Vol Flow (L s^{-1})	2.22	6.77×10^{-6}
Pump 2	Vol Flow (L s^{-1})	5.77	7.30×10^{-6}
Pump 3	Vol Flow (L s^{-1})	11.76	8.35×10^{-6}
Pump 4	Vol Flow (L s^{-1})	2.26	6.77×10^{-6}
Pump 5	Vol Flow (L s^{-1})	10.07	8.04×10^{-6}
Pump 6	Vol Flow (L s^{-1})	1.68	6.70×10^{-6}
CAPEX Component			**Total Cost ($ kg^{-1})**
ISBL			8.96×10^{-4}
OSBL			3.58×10^{-4}
C_{Eng}			1.25×10^{-4}
C_{Con}			1.88×10^{-4}

Table S11: Detailed OPEX costs for [TEA][HSO_4]

Feedstock/Utility	**Cost ($ kg^{-1})**
Sulfuric Acid	0.02
1-Methylimidazole	0.69
Water	2×10^{-4}
Steam	3×10^{-3}
Cooling Water	5.27×10^{-2}
Electricity	1.23×10^{-5}
OPEX Component	**Total Cost ($ kg^{-1})**
C_{CVP}	0.7716
C_{FCP}	0.0101

Appendix C. Environmental assessment

This appendix details the proxy data, processes and flows used in the inventory phase of LCA as well as the midpoint results from the characterization phase. For both human health and ecosystem quality expressed in biophysical units, monetization factors using the values in Table S18 were applied. Overall, the monetization proceeds as follows:

$$\text{Monetized Cost} \;=\; \sum_{i \in \text{Impacts}} \text{MF}_i \, \text{EP}_i \tag{S7}$$

where MF_i denotes the monetization factor for endpoint impact i, and EP_i the corresponding damage. Next, a currency exchange factor and inflation factor are applied to express a monetary value in USD_{2019}. For resource availability already expressed in monetary value, only an inflation factor is used for the conversion into USD_{2019}.

Uncertainty in LCA data is quantified using the Pedigree matrix approach[11], where a score $U_{\text{D},i}$ between 1 and 5 is assigned to the data based on five criteria: reliability, completeness, temporal, geographical and technological differences. All of these scores are combined with a basic uncertainty factor $U_{\text{D,b}}$ to determine the standard deviation σ_k of a log-normal distribution for each mass and energy flow k:

$$\sigma_k \;= \exp \sqrt{\ln(U_{\text{D,b}})^2 + \sum_{i=1}^{5} \ln(U_{\text{D},i})^2} \tag{S8}$$

Table S12: Proxy data used in LCI

Data Category	Proxy data	Proxy method
Air emissions	Raw materials	0.2% by mass of inflows are assumed to be vaporized or leaked
	Cooling water	4% by volume of total cooling water are assumed to be vaporized or leaked
	CO_2	90% by mass of carbon in waste stream is assumed to be completely burned in waste treatment to produce CO_2 as per the following complete combustion equation: $C_\alpha H_\beta O_\gamma + (\alpha + \frac{\beta}{4} - \frac{\gamma}{2})\, O_2 \longrightarrow \alpha CO_2 + \frac{\beta}{2}\, H_2O$
Water emissions	COD	The chemical oxygen demand (COD) or total oxygen consumed is assumed to be equivalent to the amount of oxygen needed to react with the amount of carbon remaining in the waste stream after treatment which is assumed to be 10% of total carbon
	BOD	For worst case scenario, the biological oxygen demand (BOD) which is the oxygen consumed due to biological aerobic digestion by organisms is assumed to be equivalent to the amount of COD
	TOC	The total organic carbon (TOC) which is the total amount of carbon is assumed to be equivalent to 10% of the total carbon in the waste stream which is the amount of carbon remaining after treatment
	DOC	For waste case scenario, dissolved organic carbon (DOC) is assumed to be equivalent to TOC

Table S13: 1-methylimidazole inventory

Group	**Inventory**	**Flow** (per-kg product)	**STDEV**
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.54639 m^3	1.0502
	Water, river, RER	0.27319 m^3	1.0502
	Water, well, in ground, RER	0.27319 m^3	1.0502
Inputs from technosphere (materials)	Methylamine {RER} | production | Cut-off	0.40601 kg	1.3269
	Chemical factory, organics {GLO} | market for | Cut-off	4.00×10^{-10} p	2.9905
	Heat, district or industrial, natural gas {RER} | market group for | Cut-off	6.03910 MJ	1.0502
	Electricity, medium voltage {RER} | market group for | Cut-off	0.29371 kWh	1.0502
	Heat, from steam, in chemical industry {RER} | market for heat, from steam, in chemical industry | Cut-off	0.67102 MJ	1.0502
	Glyoxal {RER} | production | Cut-off	0.7587 kg	1.3269
	Tap water {RER} | market group for | Cut-off	0.23551 kg	1.3269
	Formaldehyde {RER} | oxidation of methanol | Cut-off	0.39252 kg	1.3269
	Ammonia, liquid {RER} | ammonia production, steam reforming, liquid | Cut-off	0.22263 kg	1.3269
Emissions to air	Carbon dioxide, fossil	1.0246 kg	1.0502
	Methylamine	0.0008104 kg	1.0502
	Water/m^3	$2.232\,51 \times 10^{-5}$ m^3	1.0502
	Glyoxal	1.5144×10^{-3} kg	1.0502
	Ammonia	4.4437×10^{-4} kg	1.0502
	Formaldehyde	7.8347×10^{-4} kg	1.0502
Emissions to water	BOD5, Biological Oxygen Demand	8.2825×10^{-2} kg	1.4918
	COD, Chemical Oxygen Demand	8.2825×10^{-2} kg	1.4918
	DOC, Dissolved Organic Carbon	3.1021×10^{-2} kg	1.4918
	TOC, Total Organic Carbon	3.1021×10^{-2} kg	1.4918
	Water, RER	0.54662 m^3	1.0502
	Methylamine	9.7271×10^{-3} kg	1.0502
	Glyoxal	0.01118 kg	1.0502
	Formaldehyde	0.01373 kg	1.0502
	Ammonia	0.08065 kg	1.0502
	Imidazole	0.02934 kg	1.0502
Outputs to technosphere	Wastewater, average {Europe without Switzerland} | market for wastewater, average | Cut-off, U	0.00335 m^3	1.0502

Table S14: [HMIM][HSO_4] inventory

Group	**Inventory**	**Flow** (per-kg product)	**STDEV**
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.14759 m^3	1.0502
	Water, river, RER	0.0738 m^3	1.0502
	Water, well, in ground, RER	0.0738 m^3	1.0502
Inputs from technosphere (materials)	1-Methylimidazole	0.45657 kg	1.3269
	Chemical factory, organics {GLO} | market for | Cut-off	4.00×10^{-10} p	2.9905
	Heat, district or industrial, natural gas {RER} | market group for | Cut-off	0.84646 MJ	1.0502
	Electricity, medium voltage {RER} | market group for | Cut-off	0.00013 kWh	1.0502
	Heat, from steam, in chemical industry {RER} | market for heat, from steam, in chemical industry | Cut-off	0.09405 MJ	1.0502
	Tap water {RER} | market group for | Cut-off	0.27581 kg	1.3269
	Sulfuric acid {RER} | production | Cut-off, U	0.54543 kg	1.3269
Emissions to air	Imidazole	0.00091 kg	1.0502
	Water/m^3	$6.454\,11 \times 10^{-6}$ m^3	1.0502
	Sulfuric acid	0.00109 kg	1.0502
Emissions to water	Water, RER	0.14789 m^3	1.0502
Outputs to technosphere	Wastewater, average {Europe without Switzerland} | market for wastewater, average | Cut-off, U	2.50×10^{-5} m^3	1.0502

Table S15: [TEA][HSO_4] inventory

Group	**Inventory**	**Flow** (per-kg product)	**STDEV**
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.07003 m^3	1.0502
	Water, river, RER	0.0738 m^3	0.03502
	Water, well, in ground, RER	0.0738 m^3	0.03502
Inputs from technosphere (materials)	Triethylamine RER | production | Cut-off, U	0.50885 kg	1.3269
	Chemical factory, organics {GLO} | market for | Cut-off	4.00×10^{-10} p	2.9905
	Heat, district or industrial, natural gas {RER} | market group for | Cut-off	0.12841 MJ	1.0502
	Electricity, medium voltage {RER} | market group for | Cut-off	0.00012 kWh	1.0502
	Heat, from steam, in chemical industry {RER} | market for heat, from steam, in chemical industry | Cut-off	0.01427 MJ	1.0502
	Tap water {RER} | market group for | Cut-off	0.27104 kg	1.3269
	Sulfuric acid {RER} | production | Cut-off, U	0.49319 kg	1.3269
Emissions to air	Triethylamine	1.02×10^{-3} kg	1.0502
	Water/m^3	3.3422×10^{-6} m^3	1.0502
	Sulfuric acid	0.00098 kg	1.0502
Emissions to water	Water, RER	0.07032 m^3	1.0502
Outputs to technosphere	Wastewater, average {Europe without Switzerland} | market for wastewater, average | Cut-off, U	2.02×10^{-5} m^3	1.0502

Table S16: LCA ReCiPe midpoint results, for 1 kg of solvent

Impact indicator	**Unit**	**[TEA][HSO$_4$]**	**[HMIM][HSO$_4$]**	**Acetone**	**Glycerol**
Global warming	kg CO_2 eq	1.69209	2.72340	2.44755	3.49701
Stratospheric ozone depletion	kg CFC11 eq	3.20×10^{-7}	7.32×10^{-7}	1.20×10^{-7}	1.94×10^{-5}
Ionizing radiation	kBq Co-60 eq	0.07024	0.20873	0.02407	0.11677
Ozone formation, Human health	kg NO_x eq	0.00366	0.00397	0.00560	0.00599
Fine particulate matter formation	kg PM2.5 eq	0.00281	0.00369	0.00293	0.00513
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.00414	0.00422	0.00615	0.00628
Terrestrial acidification	kg SO_2 eq	0.00897	0.01131	0.00840	0.01505
Freshwater eutrophication	kg P eq	0.00071	0.00078	0.00030	0.00075
Marine eutrophication	kg N eq	0.00052	0.00916	1.30E-05	0.00479
Terrestrial ecotoxicity	kg 1,4-DCB eq	7.85354	9.89144	1.71027	5.52801
Freshwater ecotoxicity	kg 1,4-DCB eq	0.05117	0.08063	0.01474	0.05628
Marine ecotoxicity	kg 1,4-DCB eq	0.07388	0.10394	0.02073	0.06780
Human carcinogenic toxicity	kg 1,4-DCB eq	0.05406	0.10076	0.04632	0.06241
Human non-carcinogenic toxicity	kg 1,4-DCB eq	1.71520	2.29409	0.42870	2.89151
Land use	m^2a crop eq	0.02964	0.03823	0.00876	4.96817
Mineral resource scarcity	kg Cu eq	0.00674	0.00847	0.00125	0.00640
Fossil resource scarcity	kg oil eq	0.99145	1.18605	1.40073	0.51561
Water consumption	m^3	0.10347	0.44592	0.03007	0.05052

Table S17: LCA ReCiPe endpoint results, for 1 kg of solvent

Impact indicator	**Unit**	**[TEA][HSO$_4$]**	**[HMIM][HSO$_4$]**	**Acetone**	**Glycerol**
Human health	DALY	4.138×10^{-6}	6.700×10^{-6}	4.432×10^{-6}	7.467×10^{-6}
Ecosystem quality	species×yr	9.444×10^{-9}	1.765×10^{-8}	1.015×10^{-8}	5.920×10^{-8}
Resource availability	USD_{2013}	0.387	0.421	0.535	0.165

Table S18: Monetization, currency exchange and inflation factors

Damage area	**Unit**	**Monetization** (EUR_{2003}/DALY)	**Currency factor** (USD_{2003}/EUR_{2003})	**Inflation factor** (USD_{2019}/USD_{2003})
Human health	DALY	74,000	1.16	1.46
Ecosystem quality	species×yr	9,500,000	1.16	1.46
Resource availability	USD_{2013}	–	–	1.08

Appendix D. Additional results

This appendix presents the direct cost and environmental impacts of the solvents using biomass loading as the functional unit. The data used to convert functional unit from kg of solvent to kg of biomass are reported in Table S19.

Table S19: Biomass pretreatment data used for converting the functional unit

Solvent	**Reference**	**Biomass**	**Ratio** (kg solvent/ kg biomass)	**Fraction** (wt%)	**Recycle** (%)	**Makeup** (kg solvent/ ton biomass)
[TEA][HSO_4]	ionoSolv[3,5]	Miscanthus	5	80%	99.2%	32
[HMIM][HSO_4]	ionoSolv[3,5]	Miscanthus	5	80%	99.2%	32
Acetone	Organosolv[2]	Wood	10	70%	98%	140
Glycerol	Lynam and Coronella[7]	Rice hull	10	100%	75%	2,500

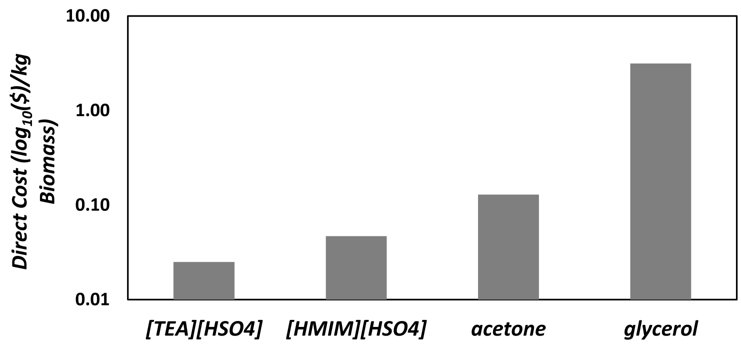

Figure S1: Direct costs of solvents per kg of treated biomass

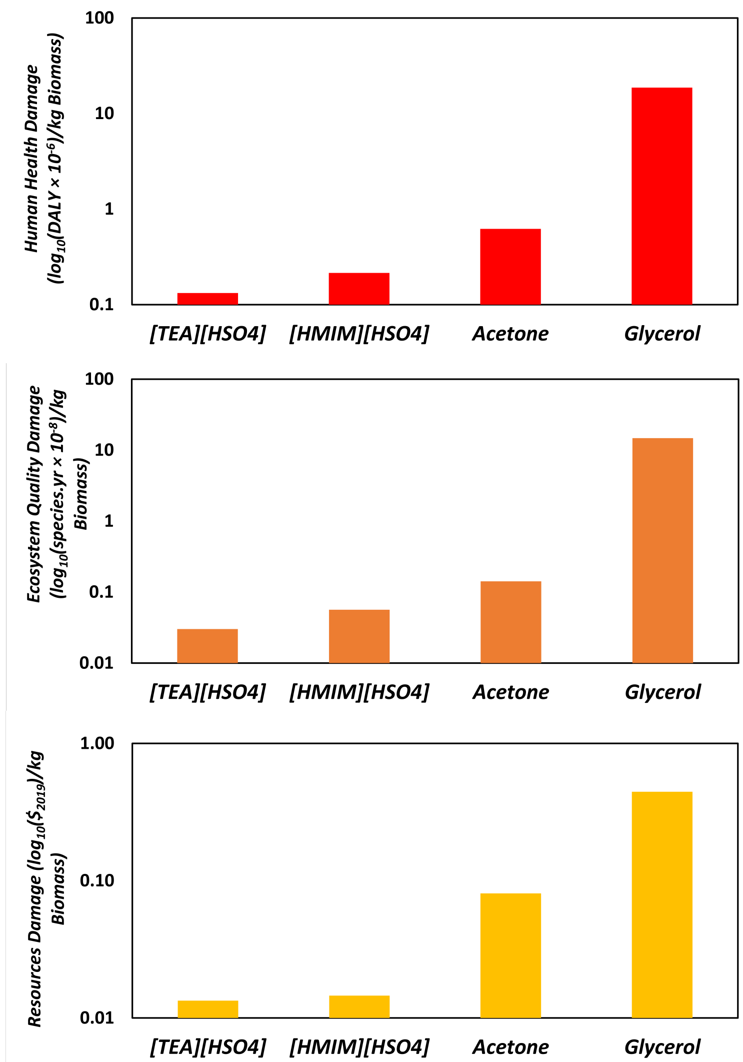

Figure S2: Endpoint environmental impacts of solvents per kg of treated biomass

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