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

$$\Delta H_f^{\circ} = \Delta H_{f}^{\circ \text{cation}} + \Delta H_{f}^{\circ \text{anion}} - \Delta H_L$$

(S1)

$\Delta H_L$ is the lattice energy calculated from Equation S2 below.

$$\Delta H_L = U_{\text{pot}} + \left[ p \left( \frac{n_m}{2} - 2 \right) + q \left( \frac{n_x}{2} - 2 \right) \right] RT$$

(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 $U_{\text{pot}}$ is calculated from Equation S3 below.

$$U_{\text{pot}} = \gamma \left( \frac{\rho_m}{M_m} \right)^{1/3} + \delta$$

(S3)

The parameters $\rho_m$ and $M_m$ denote the density and the molecular weight of the IL, respectively. The coefficients $\gamma$ and $\delta$ depend on the stoichiometry of the IL.
Table S1: 1-methylimidazole properties

| Property  | Value   | Units   |
|-----------|---------|---------|
| MW        | 82.10 g mol⁻¹ |
| BP        | 198 °C   |
| Density   | 1030 kg m⁻³ |
| ΔH_f      | 125700 kJ kmol⁻¹ |
| T_c       | 490.90 °C |
| P_c       | 6086 kPa |
| V_c       | 0.26 m³ kmol⁻¹ |
| Acentricity | 0.35 – |

Table S2: [HMIM][HSO₄] properties

| Property  | Value   | Units   |
|-----------|---------|---------|
| MW        | 180.20 g mol⁻¹ |
| BP        | 401.800 °C   |
| Density   | 1484 kg m⁻³ |
| ΔH_f      | -938000 kJ kmol⁻¹ |
| T_c       | 739.6 °C   |
| P_c       | 9189 kPa |
| V_c       | 0.43 m³ kmol⁻¹ |
| Acentricity | 0.67 – |

Table S3: [TEA][HSO₄] properties

| Property  | Value   | Units   |
|-----------|---------|---------|
| MW        | 199.30 g mol⁻¹ |
| BP        | 377.10 °C   |
| Density   | 1143 kg/m³ |
| ΔH_f      | -884100 kJ kmol⁻¹ |
| T_c       | 644.30 °C   |
| P_c       | 4732 kPa |
| V_c       | 0.62 m³ kmol⁻¹ |
| Acentricity | 0.74 – |
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.

\[ C_{ISBL} = \sum_{e \in \text{Equipment}} F_e C_e \]  

(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:

\[ C_e = a + b S^n \]  

(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:

\[ \text{Cost}_{\text{new}} = \text{Cost}_{\text{old}} + \frac{\text{Cost index}_{\text{new}}}{\text{Cost index}_{\text{old}}} \]  

(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\textsubscript{CAPEX}**

- **Fixed capital, C\textsubscript{FC}**: 
  - Onsite capital costs, ISBL 
  - Equipment cost 
  - Offsite capital costs, OSBL = 40% ISBL 
  - Engineering and construction costs, C\textsubscript{Eng} = 10%(ISBL + OSBL) 
  - Contingency charges, C\textsubscript{Con} = 15% (ISBL + OSBL)

**OPEX, C\textsubscript{OPEX}**

- **Variable cost of production, C\textsubscript{VCP}**: 
  - Raw materials, C\textsubscript{RM} 
  - Utilities, C\textsubscript{U}

- **Fixed cost of production, C\textsubscript{FCP}**: 
  - Operation labor, C\textsubscript{OL} = 720,000USD\textsubscript{2019} 
  - Supervision, C\textsubscript{Sup} = 25%C\textsubscript{OL} = 180,000USD\textsubscript{2019} 
  - Salaries, C\textsubscript{Sal} = 50%(C\textsubscript{OL} + C\textsubscript{Sup}) = 450,000USD\textsubscript{2019} 
  - Maintenance, C\textsubscript{Main} = 3%ISBL 
  - Land, C\textsubscript{Land} = 1%(ISBL + OSBL) 
  - Taxes and insurance, C\textsubscript{Tax} = 1.5%C\textsubscript{FC} 
  - General plant overhead, C\textsubscript{GPO} = 65%(C\textsubscript{OL} + C\textsubscript{Sup} + C\textsubscript{Sal} + C\textsubscript{Main})

*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\textsuperscript{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 (m³)            | 13.59                 | 2.17 × 10^{-4}          |
| Heater           | Area (m²)              | 2160.68               | 7.15 × 10^{-4}          |
| Cooler 1         | Area (m²)              | 159.45                | 7.15 × 10^{-4}          |
| Cooler 2         | Area (m²)              | 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][HSO₄]**

| Unit                  | Specifications          | Eq. Cost ($ kg⁻¹) |
|-----------------------|-------------------------|-------------------|
| Flash Tank Diameter / Length (m) | 3.55 / 12.80            | 1.48 × 10⁻⁴      |
| Reactor Volume (m³)    | 4.19                   | 1.11 × 10⁻⁴      |
| Heater Area (m²)       | 227.21                 | 8.74 × 10⁻⁴      |
| Cooler 1 Area (m²)     | 299.69                 | 8.74 × 10⁻⁴      |
| Cooler 2 Area (m²)     | 136.58                 | 8.74 × 10⁻⁴      |
| Cooler 3 Area (m²)     | 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**

| Component | Total Cost ($ kg⁻¹) |
|-----------|---------------------|
| ISBL      | 1.68 × 10⁻³         |
| OSBL      | 6.72 × 10⁻⁴         |
| £Eng      | 2.35 × 10⁻⁴         |
| £Con      | 3.53 × 10⁻⁴         |

**Table S9: Detailed OPEX costs for [HMIM][HSO₄]**

| 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**

| Component | Total Cost ($ kg⁻¹) |
|-----------|---------------------|
| £CVP      | 1.45                |
| £FCP      | 0.0108              |
### Table S10: Detailed CAPEX costs for [TEA][HSO₄]⁻

| Unit                | Specifications                  | Eq. Cost (\$ kg⁻¹) |
|---------------------|---------------------------------|--------------------|
| Flash Tank          | Diameter / Length (m) 3.21 / 11.30 | 9.08 × 10⁻⁵        |
| Reactor             | Volume (m³) 3.79                | 1.05 × 10⁻⁴        |
| Heater              | Area (m²) 191.93                | 3.36 × 10⁻⁴        |
| Cooler 1            | Area (m²) 244.19                | 3.36 × 10⁻⁴        |
| Cooler 2            | Area (m²) 133.09                | 3.36 × 10⁻⁴        |
| Cooler 3            | Area (m²) 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 × 10⁻⁵        |
| 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 |
| \(C_{\text{Eng}}\)      | 1.25 × 10⁻⁴ |
| \(C_{\text{Con}}\)      | 1.88 × 10⁻⁴ |

### Table S11: Detailed OPEX costs for [TEA][HSO₄]⁻

| 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)

| OPEX Component | Total Cost (\$ kg⁻¹) |
|----------------|---------------------|
| \(C_{\text{CVP}}\) | 0.7716             |
| \(C_{\text{FCP}}\) | 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:

\[
\text{Monetized Cost} = \sum_{i \in \text{Impacts}} \text{MF}_i \cdot \text{EP}_i
\]  
(S7)

where \(\text{MF}_i\) denotes the monetization factor for endpoint impact \(i\), and \(\text{EP}_i\) 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\(^\text{11}\), where a score \(U_{D,i}\) 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 \(U_{D,b}\) to determine the standard deviation \(\sigma_k\) of a log-normal distribution for each mass and energy flow \(k\):

\[
\sigma_k = \exp \sqrt{\ln(U_{D,b})^2 + \sum_{i=1}^{5} \ln(U_{D,i})^2}
\]  
(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                                                                                                                                      |
|                   | CO₂         | 90% by mass of carbon in waste stream is assumed to be completely burned in waste treatment to produce CO₂ as per the following complete combustion equation: $C_{\alpha}H_{\beta}O_{\gamma} + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)O_2 \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O$ |
| 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 m³ | 1.0502 |
| Water, river, RER            | 0.27319 m³ | 1.0502 |
| Water, well, in ground, RER  | 0.27319 m³ | 1.0502 |
| Methylamine \{RER\} | production | Cut-off | 0.40601 kg | 1.3269 |
| Chemical factory, organics \{GLO\} | market for | Cut-off | $4.00 \times 10^{-10}$ | 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 |
| Inputs from technosphere (materials) | 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/m³                    |                                                                           | $2.23251 \times 10^{-5}$ m³ | 1.0502 |
| Glyoxal                     |                                                                           | $1.544 \times 10^{-3}$ kg | 1.0502 |
| Ammonia                     |                                                                           | $4.443 \times 10^{-4}$ kg | 1.0502 |
| Formaldehyde                 |                                                                           | $7.8347 \times 10^{-4}$ kg | 1.0502 |
| Emissions to water           |                                                                           |                        |       |
| BOD5, Biological Oxygen Demand |                                                                           | $8.2825 \times 10^{-2}$ kg | 1.4918 |
| COD, Chemical Oxygen Demand  |                                                                           | $8.2825 \times 10^{-2}$ kg | 1.4918 |
| DOC, Dissolved Organic Carbon |                                                                           | 3.1021 \times 10^{-2} kg | 1.4918 |
| TOC, Total Organic Carbon   |                                                                           | 3.1021 \times 10^{-2} kg | 1.4918 |
| Water, RER                  |                                                                           | 0.54662 m³ | 1.0502 |
| Methylamine                 |                                                                           | 9.7271 \times 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 m³ | 1.0502 |
Table S14: [HMIM][HSO₄] inventory

| Group                     | Inventory                                           | Flow (per-kg product) | STDEV  |
|---------------------------|-----------------------------------------------------|-----------------------|--------|
| Inputs from nature        | Water, cooling, unspecified natural origin, RER     | 0.14759 m³            | 1.0502 |
|                           | Water, river, RER                                   | 0.0738 m³             | 1.0502 |
|                           | Water, well, in ground, RER                         | 0.0738 m³             | 1.0502 |
| Inputs from technosphere  | 1-Methylimidazole                                   | 0.45657 kg            | 1.3269 |
| (materials)               | 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/m³                                            | 6.45411 × 10⁻⁶ m³     | 1.0502 |
|                           | Sulfuric acid                                       | 0.00109 kg            | 1.0502 |
| Emissions to water        | Water, RER                                          | 0.14789 m³            | 1.0502 |
| Outputs to technosphere   | Wastewater, average {Europe without Switzerland} |                     |        |
|                           | market for wastewater, average | Cut-off, U | | 2.50 × 10⁻⁵ m³ | 1.0502 |
Table S15: [TEA][HSO₄] inventory

| Group                     | Inventory                                                                 | Flow (per-kg product) | STDEV  |
|---------------------------|---------------------------------------------------------------------------|-----------------------|--------|
| Inputs from nature        | Water, cooling, unspecified natural origin, RER                           | 0.07003 m³            | 1.0502 |
|                           | Water, river, RER                                                          | 0.0738 m³             | 0.03502 |
|                           | Water, well, in ground, RER                                                | 0.0738 m³             | 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/m³                                                                   | 3.3422 × 10^{-6} m³  | 1.0502 |
|                           | Sulfuric acid                                                              | 0.00098 kg           | 1.0502 |
| Emissions to water        | Water, RER                                                                 | 0.07032 m³            | 1.0502 |
| Outputs to technosphere   | Wastewater, average {Europe without Switzerland} | market for wastewater, average | Cut-off, U | 2.02 × 10^{-5} m³ | 1.0502 |
Table S16: LCA ReCiPe midpoint results, for 1 kg of solvent

| Impact indicator                  | Unit           | [TEA][HSO₄] | [HMIM][HSO₄] | Acetone | Glycerol |
|----------------------------------|----------------|-------------|--------------|---------|----------|
| Global warming                   | kg CO₂ 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 NOₓ 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 NOₓ eq | 0.00414 | 0.00422 | 0.00615 | 0.00628 |
| Terrestrial acidification        | kg SO₂ 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                         | m²a 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                | m³             | 0.10347     | 0.44592      | 0.03007 | 0.05052  |

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

| Impact indicator                  | Unit           | [TEA][HSO₄] | [HMIM][HSO₄] | 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            | USD₂₀¹³       | 0.387       | 0.421        | 0.535   | 0.165    |
Table S18: Monetization, currency exchange and inflation factors

| Damage area           | Unit       | Monetization \((\text{EUR}_{2003}/\text{DALY})\) | Currency factor \((\text{USD}_{2003}/\text{EUR}_{2003})\) | Inflation factor \((\text{USD}_{2019}/\text{USD}_{2003})\) |
|-----------------------|------------|-----------------------------------------------|------------------------------------------------|------------------------------------------------|
| 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][HSO₄]        | ionoSolv³,⁵        | Miscanthus   | 5                             | 80%            | 99.2%       | 32                              |
| [HMIM][HSO₄]       | ionoSolv³,⁵        | Miscanthus   | 5                             | 80%            | 99.2%       | 32                              |
| Acetone            | Organosolv²        | Wood         | 10                            | 70%            | 98%         | 140                             |
| Glycerol           | Lynam and Coronella⁷ | 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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