Environmental Sustainability of Cellulose-Supported Solid Ionic Liquids for CO_2 Capture

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Supporting information

S1. Estimation of raw material requirements

Table S1 Raw materials used in the synthesis of the SoILs and their precursors

Compound	Formula	MW (g·mol^{-1})
[N_{1888}][Ac]	$C_{27}H_{57}NO_2$	427
[N_{1888}][OH]	$C_{25}H_{55}NO$	385
Acetic acid	CH_3COOH	60
Water	H_2O	18
[N_{1888}]I	$C_{25}H_{54}NI$	495
Trioctylamine	$C_{24}H_{51}N$	353
Methyl iodide	CH_3I	142
1-octanol	$C_8H_{17}OH$	130
Ammonia	NH_3	17
[N_{4444}][Ac]	$C_{18}H_{39}NO_2$	301
[N_{4444}][OH]	$C_{16}H_{37}NO$	259
[N_{4444}]Br	$C_{16}H_{36}NBr$	322
Tributylamine	$C_{12}H_{27}N$	185
1-bromobutane	C_4H_9Br	137
1-butanol	C_4H_9OH	74
[N_{8888}][Br]	$C_{32}H_9Br$	546
1-bromooctane	$C_8H_{17}Br$	193
[Bmim]Br	$C_8H_{15}N_2Br$	219
1-methylimidazole	$C_4H_6N_2$	82

S1.1. Production of [N_{1888}][Ac]

$$[N_{1888}][OH] + CH_3COOH \rightarrow [N_{1888}][Ac] + H_2O$$

$$1000\ g\ [N_{1888}][Ac] \times \frac{1\ mol\ [N_{1888}][Ac]}{427\ g\ [N_{1888}][Ac]} \times \frac{1\ mol\ [N_{1888}][OH]}{1\ mol\ [N_{1888}][Ac]} \times \frac{385\ g\ [N_{1888}][OH]}{1\ mol\ [N_{1888}][OH]} = \mathbf{901.6\ g\ [N_{1888}][OH]}$$

$$1000\ g\ [N_{1888}][Ac] \times \frac{1\ mol\ [N_{1888}][Ac]}{427\ g\ [N_{1888}][Ac]} \times \frac{1\ mol\ CH_3COOH}{1\ mol\ [N_{1888}][Ac]} \times \frac{60\ g\ CH_3COOH}{1\ mol\ CH_3COOH} = \mathbf{140.5\ g\ CH_3COOH}$$

$$1000\ g\ [N_{1888}][Ac] \times \frac{1\ mol\ [N_{1888}][Ac]}{427\ g\ [N_{1888}][Ac]} \times \frac{1\ mol\ H_2O}{1\ mol\ [N_{1888}][Ac]} \times \frac{18\ g\ H_2O}{1\ mol\ H_2O} = \mathbf{42.1\ g\ H_2O}$$

$\mathbf{[N_{1888}][OH]}$ is produced from $[N_{1888}][I]$ using an anion exchange resin (AER):
$[N_{1888}]I \xrightarrow{AER} [N_{1888}][OH]$

For the production of $[N_{1888}][Ac]$ we need 1 mole of $[N_{1888}][OH]$ or 1 mole of $[N_{1888}][I]$; therefore:

$$901.6\ g\ [N_{1888}][OH] \times \frac{1\ mol\ [N_{1888}][OH]}{385\ g\ [N_{1888}][OH]} \times \frac{1\ mol\ [N_{1888}][I]}{1\ mol\ [N_{1888}][OH]} \times \frac{495\ g\ [N_{1888}][I]}{1\ mol\ [N_{1888}][I]} = \mathbf{1159.2\ g\ [N_{1888}][I]}$$

S1.1.1. Production of [N_{1888}][I]

$(C_8H_{17})_3N + CH_3I \rightarrow [N_{1888}]I$

$$1000\ g\ [N_{1888}][I] \times \frac{1\ mol\ [N_{1888}][I]}{495\ g\ [N_{1888}][I]} \times \frac{1\ mol\ (C_8H_{17})_3N}{1\ mol\ [N_{1888}][I]} \times \frac{353\ g\ (C_8H_{17})_3N}{1\ mol\ (C_8H_{17})_3N} = \mathbf{713.1\ g\ (C_8H_{17})_3N}$$

$$1000\ g\ [N_{1888}][I] \times \frac{1\ mol\ [N_{1888}][I]}{495\ g\ [N_{1888}][I]} \times \frac{1\ mol\ CH_3I}{1\ mol\ [N_{1888}][I]} \times \frac{142\ g\ CH_3I}{1\ mol\ CH_3I} = \mathbf{286.9\ g\ CH_3I}$$

S1.1.2. Production of $(C_8H_{17})_3N$

$3C_8H_{17}OH + NH_3 \rightarrow (C_8H_{17})_3N + 3H_2O$

$$1000\ g\ (C_8H_{17})_3N \times \frac{1\ mol\ (C_8H_{17})_3N}{353\ g\ (C_8H_{17})_3N} \times \frac{3\ mol\ C_8H_{17}OH}{1\ mol\ (C_8H_{17})_3N} \times \frac{130\ g\ C_8H_{17}OH}{1\ mol\ C_8H_{17}OH} = \mathbf{1104.8\ g\ C_8H_{17}OH}$$

$$1000\ g\ (C_8H_{17})_3N \times \frac{1\ mol\ (C_8H_{17})_3N}{353\ g\ (C_8H_{17})_3N} \times \frac{1\ mol\ NH_3}{1\ mol\ C_8H_{17}OH} \times \frac{17\ g\ NH_3}{1\ mol\ NH_3} = \mathbf{48.2\ g\ NH_3}$$

$$1000\ g\ (C_8H_{17})_3N \times \frac{1\ mol\ (C_8H_{17})_3N}{353\ g\ (C_8H_{17})_3N} \times \frac{3\ mol\ H_2O}{1\ mol\ (C_8H_{17})_3N} \times \frac{18\ g\ H_2O}{1\ mol\ H_2O} = \mathbf{153.0\ g\ H_2O}$$

S1.2. Production of $[N_{4444}][Ac]$

$[N_{4444}][OH] + CH_3COOH \rightarrow [N_{4444}][Ac] + H_2O$

$$1000\ g\ [N_{4444}][Ac] \times \frac{1\ mol\ [N_{4444}][Ac]}{301\ g\ [N_{4444}][Ac]} \times \frac{1\ mol\ [N_{4444}][OH]}{1\ mol\ [N_{4444}][Ac]} \times \frac{259\ g\ [N_{4444}][OH]}{1\ mol\ [N_{4444}][OH]} = \mathbf{860.47\ g\ [N_{4444}][OH]}$$

$$1000\ g\ [N_{4444}][Ac] \times \frac{1\ mol\ [N_{4444}][Ac]}{301\ g\ [N_{4444}][Ac]} \times \frac{1\ mol\ CH_3COOH}{1\ mol\ [N_{4444}][Ac]} \times \frac{60\ g\ CH_3COOH}{1\ mol\ CH_3COOH} = \mathbf{199.34\ g\ CH_3COOH}$$

$$1000\ g\ [N_{4444}][Ac] \times \frac{1\ mol}{301\ g} \times \frac{1\ mol\ H_2O}{1\ mol\ [N_{4444}][Ac]} \times \frac{18\ g\ H_2O}{1\ mol\ H_2O} = \mathbf{59.80\ g\ H_2O}$$

$[\boldsymbol{N_{4444}}][\boldsymbol{OH}]$ is produced from $[N_{4444}][Br]$ using an Anion Exchange Resin (AER):
$[N_{4444}][Br] \xrightarrow{AER} [N_{4444}][OH]$

For the production of $[N_{4444}][Ac]$ we need 1 mole of $[N_{4444}][OH]$ or 1 mole of $[N_{4444}][Br]$; therefore:

$$860.47\ g\ [N_{4444}][OH] \times \frac{1\ mol\ [N_{4444}][OH]}{259\ g\ [N_{4444}][OH]} \times \frac{1\ mol\ [N_{4444}][Br]}{1\ mol\ [N_{4444}][OH]} \times \frac{322\ g\ [N_{4444}][Br]}{1\ mol\ [N_{4444}][Br]} = \mathbf{1069.77\ g\ [N_{4444}][Br]}$$

S1.2.1. Production of $[N_{4444}][Br]$

$(C_4H_9)_3N + C_4H_9Br \rightarrow [N_{4444}]Br$

$$1000\ g\ [N_{4444}][Br] \times \frac{1\ mol\ [N_{4444}][Br]}{322\ g\ [N_{4444}][Br]} \times \frac{1\ mol\ (C_4H_9)_3N}{1\ mol\ [N_{4444}][Br]} \times \frac{185\ g\ (C_4H_9)_3N}{1\ mol (C_4H_9)_3N} = \mathbf{574.53\ g\ (C_4H_9)_3N}$$

$$1000\ g\ [N_{4444}][Br] \times \frac{1\ mol\ [N_{4444}][Br]}{322\ g\ [N_{4444}][Br]} \times \frac{1\ mol\ C_4H_9Br}{1\ mol\ [N_{4444}][Br]} \times \frac{137\ g\ C_4H_9Br}{1\ mol\ C_4H_9Br} = \mathbf{425.46\ g\ C_4H_9Br}$$

S1.2.2. Production of $(C_4H_9)_3N$

$3C_4H_9OH + NH_3 \rightarrow (C_4H_9)_3N + 3H_2O$

$$1000\ g\ (C_4H_9)_3N \times \frac{1\ mol\ (C_4H_9)_3N}{185\ g\ (C_4H_9)_3N} \times \frac{3\ mol\ C_4H_9OH}{1\ mol\ (C_4H_9)_3N} \times \frac{74\ g\ C_4H_9OH}{1\ mol\ C_4H_9OH} = \mathbf{1200.0\ g\ C_4H_9OH}$$

$$1000\ g\ (C_4H_9)_3N \times \frac{1\ mol\ (C_4H_9)_3N}{185\ g\ (C_4H_9)_3N} \times \frac{1\ mol\ NH_3}{1\ mol\ C_4H_9OH} \times \frac{17\ g\ NH_3}{1\ mol\ NH_3} = \mathbf{91.89 g\ NH_3}$$

$$1000\ g\ \ (C_4H_9)_3N\ \times \frac{1\ mol\ (C_4H_9)_3N}{185\ g\ (C_4H_9)_3N} \times \frac{3\ mol\ H_2O}{1\ mol\ (C_4H_9)_3N} \times \frac{18\ g\ H_2O}{1\ mol\ H_2O} = \mathbf{291.89\ g\ H_2O}$$

S1.3. Production of $[N_{8888}][Br]$

$(C_8H_{17})_3N + C_8H_{17}Br \rightarrow [N_{8888}]Br$

$$1000\ g\ [N_{8888}][Br] \times \frac{1\ mol\ [N_{8888}][Br]}{546\ g\ [N_{8888}][Br]} \times \frac{1\ mol\ (C_8H_{17})_3N}{1\ mol\ [N_{8888}][Br]} \times \frac{353\ g\ (C_8H_{17})_3N}{1\ mol\ (C_8H_{17})_3N} = \mathbf{646.5\ g\ (C_8H_{17})_3N}$$

$$1000\ g\ [N_{8888}][Br] \times \frac{1\ mol\ [N_{8888}][Br]}{546\ g\ [N_{8888}][Br]} \times \frac{1\ mol\ C_8H_{17}Br}{1\ mol\ [N_{8888}][Br]} \times \frac{193\ g\ C_8H_{17}Br}{1\ mol\ \ C_8H_{17}Br} = \mathbf{353.5\ g\ C_8H_{17}Br}$$

S1.4. [Bmim]Br

$C_4H_6N_2 + C_4H_9Br \rightarrow [Bmim]Br$

$$1000\ g\ [Bmim]Br \times \frac{1\ mol\ [Bmim]Br}{219\ g\ [Bmim]Br} \times \frac{1\ mol\ C_4H_6N_2}{1\ mol\ [Bmim]Br} \times \frac{82\ g\ C_4H_6N_2}{1\ mol\ C_4H_6N_2} = \mathbf{374.7\ g\ C_4H_6N_2}$$

$$1000\ g\ [Bmim]Br \times \frac{1\ mol\ [Bmim]Br}{219\ g\ [Bmim]Br} \times \frac{1\ mol\ C_4H_9Br}{1\ mol\ [Bmim]Br} \times \frac{137\ g\ \ C_4H_9Br}{1\ mol\ C_4H_9Br} = \mathbf{625.3\ g\ C_4H_9Br}$$

S2. Estimation of energy requirements

The energy requirements for the production of the SoILs and their precursors have been estimated using the heat of formation of the reactants and products. This methodology is based on the assumption that the heat required by the reactor is equal to the enthalpy of reaction assuming that no work is carried and that the kinetic and potential energy are zero, according to:

$$Q - W = \Delta H + \Delta E_k + \Delta E_p$$

If W, ΔE_k and ΔE_p are zero, then:

$$Q = \Delta H$$

where:

Q reactor heat consumption
W work
ΔH enthalpy of reaction
ΔE_k kinetic energy
ΔE_p potential energy

The enthalpy of reaction ΔH can be calculated as:

$$\Delta H = \sum (n \cdot H)out - \sum (n \cdot H)in$$

where:

n molecular weight of reactants
H specific enthalpy of reactants

The specific enthalpy of reactants is equal to:

$$H = \Delta H_f^0 + \int_{T_1}^{T_2} C_p dT$$

where:

ΔH_f^0 heat of formation of reactants
C_p calorific value of reactants
T_1,T_2 reference temperature (25 ºC) and temperature of the reactants, respectively.

Table S2 Thermodynamic properties of the compounds used in the synthesis of the SoILs and their precursors

Compound	**Formula**	**Cp (kJ·mol^{-1}K^{-1})**	**ΔH°$_f$ (kJ·mol^{-1})**	**Assumptions**	**Source**
[N$_{1888}$][Ac]	$C_{27}H_{57}NO_2$	-	-615	ΔH°$_f$ of ammonium acetate used as proxy	Aspen Plus[1]
[N$_{1888}$][OH]	$C_{25}H_{55}NO$	-	-498.6	ΔH°$_f$ of tetra-n-butylammonium iodide used as proxy	NIST[2]
Acetic acid	CH_3COOH	-	-484.5		HSC Chemistry[3]
Water	H_2O	0.03	-285.8		HSC Chemistry[3]
[N$_{1888}$]I	$C_{25}H_{54}NI$	-	-498.6	ΔH°$_f$ of tetra-n-butylammonium iodide used as proxy	NIST[2]
Trioctylamine	$C_{24}H_{51}N$	0.87	-585.3		Aspen Plus[1]
Methyl iodide	CH_3I	-	-13.6		Aspen Plus[1]
1-octanol	$C_8H_{17}OH$	0.41	-426.60		Aspen Plus[1]
Ammonia	NH_3	0.04	-45.94		Aspen Plus[1]
[N$_{4444}$][Ac]	$C_{18}H_{39}NO_2$	-	-615	ΔH°$_f$ of ammonium acetate used as proxy	Aspen Plus[1]
[N$_{4444}$][OH]	$C_{16}H_{37}NO$	-	-540.3	ΔH°$_f$ of tetra-n-butylammonium bromide used as proxy	NIST[4]
[N$_{4444}$]Br	$C_{16}H_{36}NBr$	-	-540		NIST[4]
Tributylamine	$C_{12}H_{27}N$	0.47	-327		Aspen Plus[1]
1-bromobutane	C_4H_9Br	0.17	-148		Aspen Plus[1]
1-butanol	C_4H_9OH	0.26	-327		Aspen Plus[1]
[N$_{8888}$][Br]	$C_{32}H_9Br$	-	-540.3	ΔH°$_f$ of tetra-n-butylammonium bromide used as proxy	NIST[4]
1-bromooctane	$C_8H_{17}Br$	-	-245.2		Aspen Plus[1]
[Bmim]Br	$C_8H_{15}N_2Br$	0.35	-178		Cp: Aspen Plus[1] ΔH°$_f$: Paulechka et al.[5]
1-methylimidazole	$C_4H_6N_2$	0.19	70.7		Aspen Plus[1]

S3. Comparison of SoILs

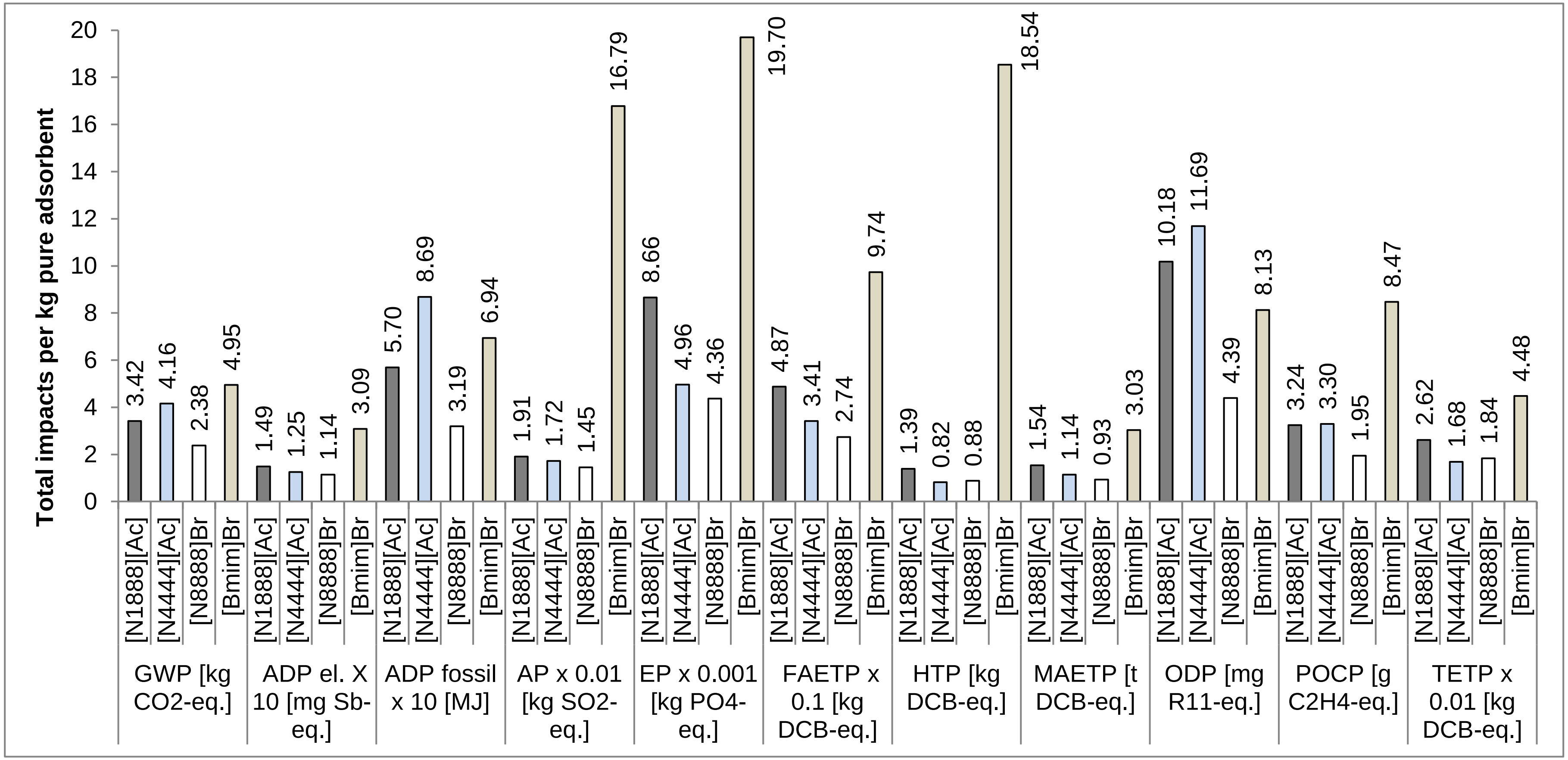

Figure S1. Life cycle environmental impacts of the pure SoILs considered in the study.
(The impacts expressed per kg of pure adsorbent. For impacts nomenclature see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)

S4. Sensitivity analysis

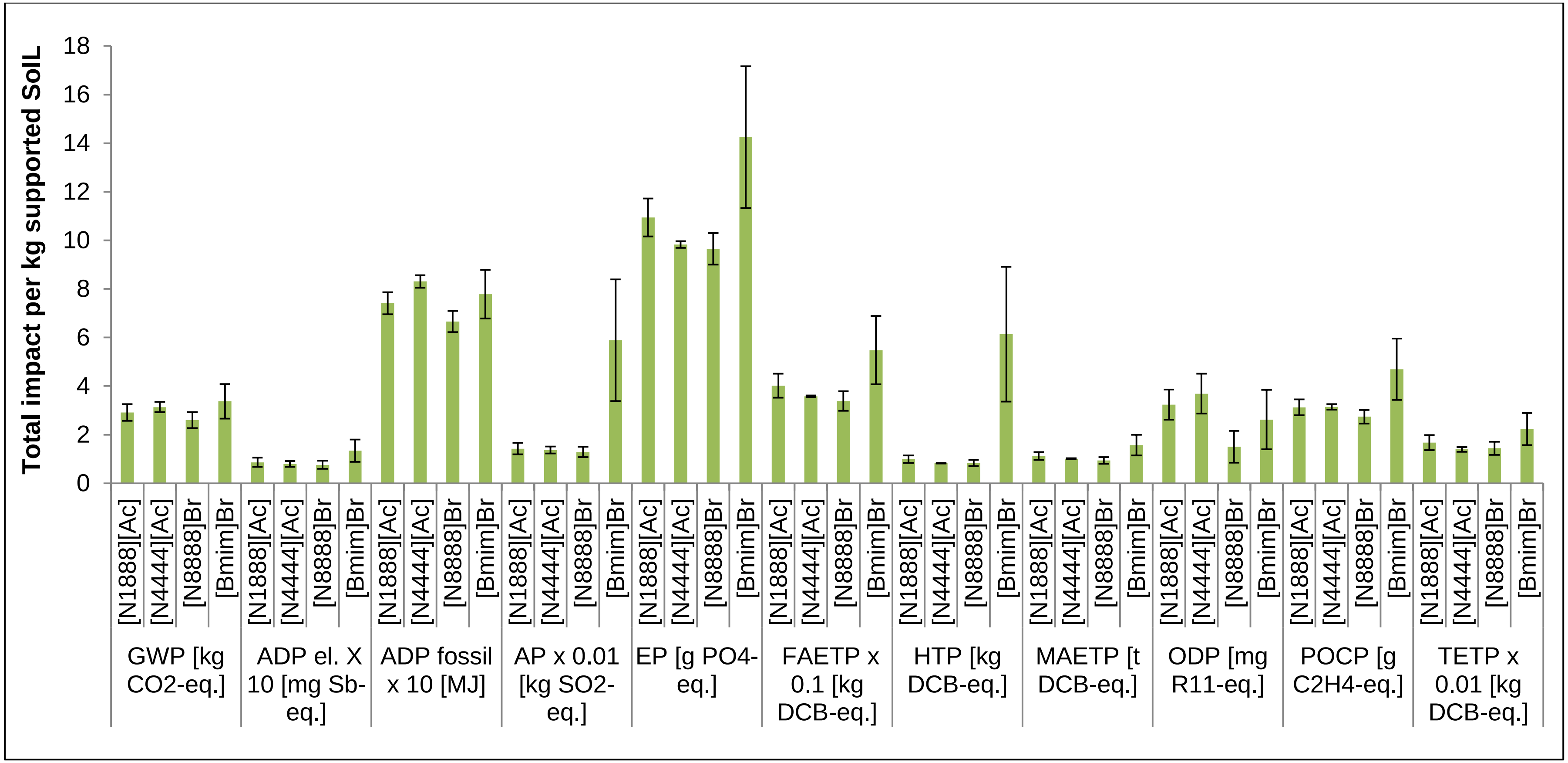

Figure S2. Sensitivity analysis for the assumptions on the raw materials used in the production of the SoILs with 70% cellulose loading

(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)

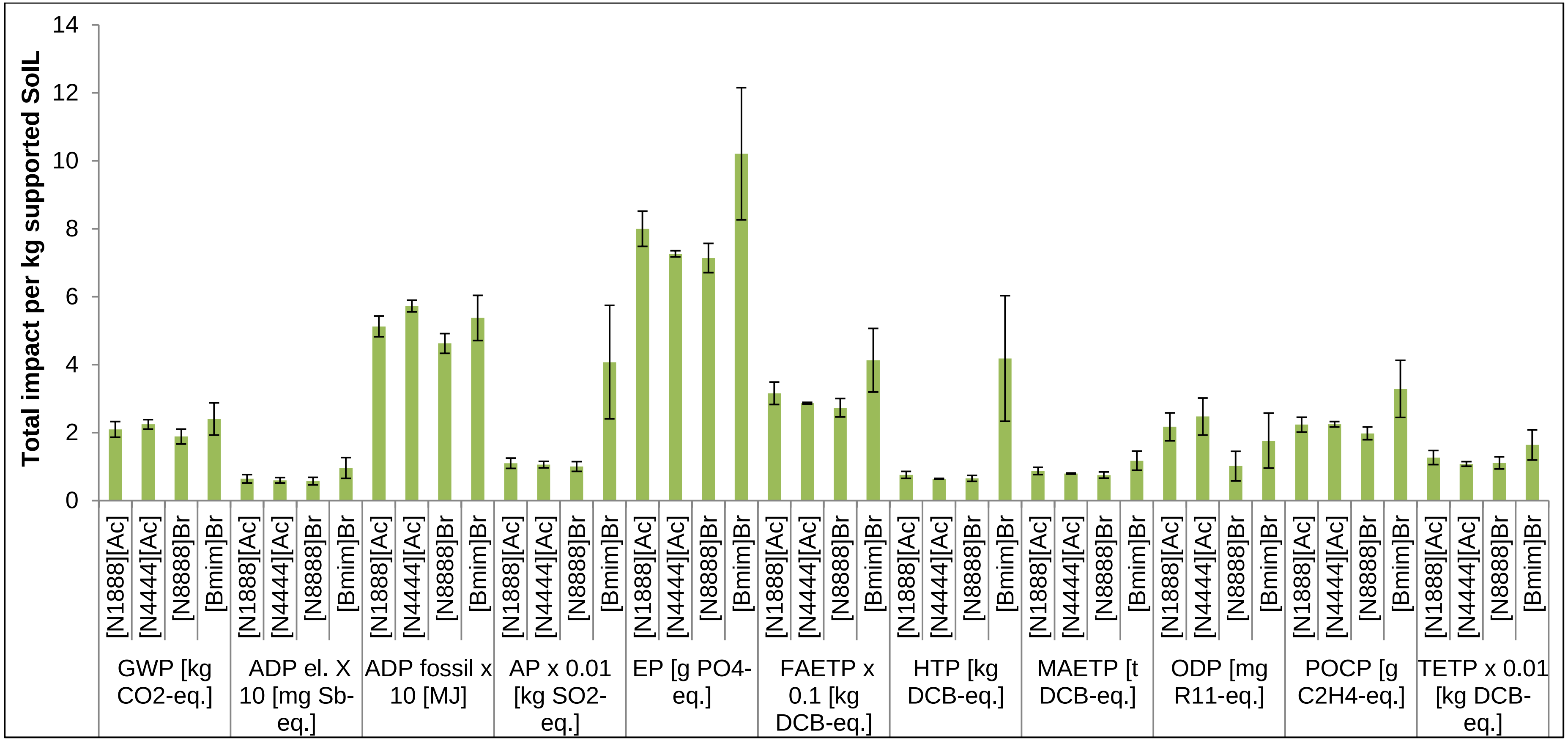

Figure S3. Sensitivity analysis for the assumptions on the raw materials used in the production of the SoILs with 80% cellulose loading
(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)

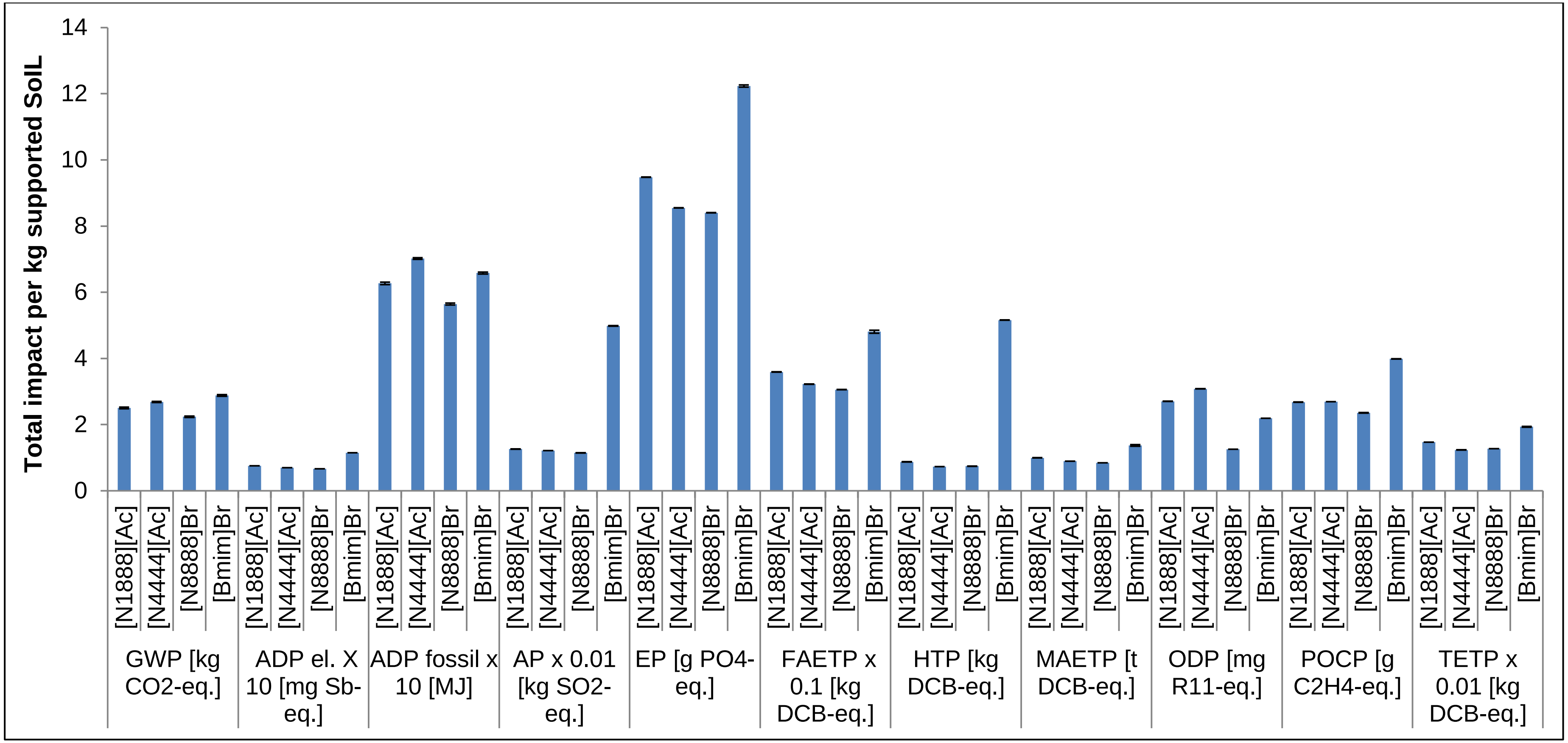

Fig. S4 Sensitivity analysis for the assumptions on the energy required in the production of the SoILs with 75% cellulose loading.

(The graph bars represent the impacts in the base case and the error bars the impacts for the ± variation in impacts of the proxy raw materials. For impacts nomenclature, see Section 3.1 in the paper. Some impacts have been scaled to fit – to obtain the original values, multiply by the factor shown on the x-axis.)

References

1. Aspen Technology. (2013). Aspen Plus Version 8.4. Burlington, MA, USA.
2. NIST. Tetra-n-butylammonium iodide. National Institute of Standards and Technology. (2016). http://webbook.nist.gov/cgi/cbook.cgi?ID=C311284&Units=SI&Mask=7.
3. Outotec Oyj. (2002). HSC Chemistry Version 5.1. Espoo, Finland
4. NIST. Tetra-N-butylammonium bromide. National Institute of Standards and Technology. (2016). http://webbook.nist.gov/cgi/inchi?ID=C1643192&Mask=1.
5. Paulechka, Y. U., Kabo, A. G. & Blokhin, A. V. (2009). Calorimetric Determination of the Enthalpy of 1-Butyl-3-methylimidazolium Bromide Synthesis: A Key Quantity in Thermodynamics of Ionic Liquids. *J. Phys. Chem. B* **113,** 14742–14746 (2009).