A novel methodology for assessing the environmental sustainability of ionic liquids used for CO_2 capture

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1. Estimation of material requirements

This section details the estimations of the quantities of the raw materials used for the synthesis ($[P_{66614}][124Triz]$) shown in Table 3 in the paper. The raw materials and their molecular weights are listed in Table S1.

Chamical compound	Chemical	Molecular weight
chemical compound	formula	(g/mol)
[P ₆₆₆₁₄][124Triz]	$C_{34}H_{71}PN_3$	552
[P ₆₆₆₁₄]Cl	C ₃₂ H ₆₈ CIP	519
[P ₆₆₆₁₄][OH]	C ₃₂ H ₆₈ OHP	500
1,2,4-triazole	$C_2H_3N_3$	69
1-chlorotetradecane	C ₁₄ H ₂₉ Cl	233
1-hexene	C ₆ H ₁₂	84
1-tetradecanol	C ₁₄ H ₃₀ O	214
Ammonia	NH ₃	17
Ammonium formate	NH ₄ HCO ₂	63
Anion exchange resin	ŘΟΗ ⁻	
Ditetradecyl carbonate	$C_{29}H_{58}O_3$	454
Ditetradecyl ether	C ₂₈ H ₅₈ O	410
Formamide	CH₃NO	45
Formic acid	CH_2O_2	46
Hydrazine hydrate	$N_2H_4 \cdot H_2O$	50
Hydrochloric acid	HCI	36
Phosgene	COCI ₂	99
Phosphine	PH₃	35
Trihexylphosphine	C ₁₈ H ₃₉ P	287
Water	H ₂ O	18

Table S1 Raw materials used in the	synthesis of [P ₆₆₆₁₄][124Triz] and its precursors
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1.1 <u>Trihexyl(tetradecyl)phosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz])</u>

The calculations for the production of 1000 g of $[P_{66614}]$ [124Triz] are shown below:

 $\frac{1000 \text{ g } [P66614][124 \text{ Triz}]}{552 \text{ g/mol}} = 1.81 \text{ moles } [P66614][124 \text{ Triz}]$

 $1.81 \ C_{32}H_{68}OHP \ + \ 1.81 \ C_{2}H_{3}N_{3} \rightarrow \ 1.81 \ C_{34}H_{71}PN_{3} \ + \ 1.81 \ OH^{-1}$

Therefore:

1.81 moles [P66614][OH] × 500 $\frac{g}{mol}$ = 905 g [P66614][OH]

1.81 moles 1,2,4 triazole × $69 \frac{g}{mol}$ = 124.89 g 1,2,4 triazole

1.81 moles $OH^- \times 17 \frac{g}{mol} = 30 \text{ g } OH^-$

1.2 <u>Trihexyl(tetradecyl)phosphonium hydroxide ([P₆₆₆₁₄][OH])</u>

The calculations for the production of 905 g (1.81 moles) of [P₆₆₆₁₄][OH] are as follows:

$$1.81 \text{ } \text{C}_{32}\text{H}_{68}\text{CIP} + \bar{\text{R}}\text{OH}^{-} \rightarrow 1.81 \text{ } \text{C}_{32}\text{H}_{68}\text{OHP} + 1.81 \text{ } \bar{\text{R}}\text{CI}^{-}$$

Hence:

1.81 moles [P66614]Cl × 519 $\frac{g}{mol}$ = 940 g [P66614]Cl

1.81 mol Cl⁻ × 35.5 $\frac{g}{mol}$ = 64.3 g Cl⁻

1.3 <u>Trihexyl(tetradecyl)phosphonium chloride ([P₆₆₆₁₄]Cl)</u>

940 g (1.81 moles) of [P₆₆₆₁₄]Cl is produced according to the following reaction:

 $2 C_{14}H_{29}CI + 2 C_{18}H_{39}P \rightarrow 1.81 C_{32}H_{68}CIP + 0.083 HCI + waste$

Thus:

2 moles chlorotetradecane × $233 \frac{g}{mol}$ = 466 g chlorotetradecane

2 moles trihexylphosphine × 287 $\frac{g}{mol}$ = 574 g trihexylphosphine

0.083 moles HCl × $36 \frac{g}{mol}$ = 2.98 g HCl

(466 + 574) g of reactants -(940 + 2.98) g of products = 97.02 g of waste

The produced waste stream contains unreacted raw materials and traces of other intermediate species.¹

1.4 Trihexylphosphine

The calculations for the production of 574 g (2 moles) of trihexylphosphine are shown below:

 $2.4 \ \text{PH}_3 + 7.2 \ \text{C}_6\text{H}_{12} \rightarrow 2 \ \text{C}_{18}\text{H}_{39}\text{P} + 0.4 \ \text{PH}_3 + 1.2 \ \text{C}_6\text{H}_{12}$

Therefore:

2.4 moles phosphine × $35\frac{g}{mol}$ = 84 g phosphine

- 7.2 moles hexene × $84 \frac{g}{mol}$ = 604.8 g hexene
- 0.4 moles phosphine × $35\frac{g}{mol}$ = 14 g phosphine
- 1.2 moles hexene × $84 \frac{g}{mol}$ = 100.8 g hexene
- 1.5 <u>1-Chlorotetradecane</u>

The production of 466 g (2 moles) of 1-chlorotetradecane proceeds according to the following two-step reaction:

i) 2.2 $C_{14}H_{30}O$ + 1.5 HCl \rightarrow 1.5 $C_{14}H_{29}Cl$ + 0.6 $C_{14}H_{30}O$ + 0.04 $C_{28}H_{58}O$ + 1.7 H_2O

ii) 1.5 $C_{14}H_{29}CI + 0.6 C_{14}H_{30}O + 0.04 C_{28}H_{58}O + 1.1 COCI_2 \rightarrow 2 C_{14}H_{29}CI + 0.04 C_{28}H_{58}O + 0.07 C_{29}H_{58}O_3 + 0.7 HCI + 0.6 COCI_2$

Hence:

2.2 moles tetradecanol × 214 $\frac{g}{mol}$ = 470.8 g tetradecanol 1.5 moles HCl × 36 $\frac{g}{mol}$ = 54 g HCl 1.5 moles chlorotetradecane × 233 $\frac{g}{mol}$ = 349.5 g chlorotetradecane 0.6 moles chlorotetradecane × 214 $\frac{g}{mol}$ = 128.4 g tetradecanol 0.04 moles ditetradecyl ether × 410 $\frac{g}{mol}$ = 16.4 g ditetradecyl ether 1.7 moles water × 18 $\frac{g}{mol}$ = 30.7 g water 1.1 moles phosgene × 99 $\frac{g}{mol}$ = 108.9 g phosgene 0.07 moles ditetradecyl carbonate × 454 $\frac{g}{mol}$ = 31.8 g ditetradecyl carbonate 0.73 moles HCl × 36 $\frac{g}{mol}$ = 26.3 g HCl 0.64 moles phosgene × 99 $\frac{g}{mol}$ = 63.4 g phosgene 1.6 <u>1.2.4-Triazole</u> The calculations for the production of 125 g (1.81 moles) of 1.2.4-triazole are shown below:

 $8.3\ CH_3NO$ + 3.24 $N_2H_4\cdot H_2O$ \rightarrow 1.81 $C_2H_3N_3$ + 0.86 CH_3NO + 1.25 N_2H_4 + 2.35 NH_3 + 1.9 CH_2O_2 + 5 H_2O + 0.74 NH_4HCO_2 + waste

Hence:

8.3 moles formamide × $45 \frac{g}{mol}$ = 373.5 g formamide

3.24 moles hydrazine hydrate × $50 \frac{g}{mol}$ = 162 g hydrazine hydrate

- 0.86 moles formamide $\times 45 \frac{g}{mol} = 38.7 \text{ g}$ formamide
- 1.25 moles hydrazine × $32 \frac{g}{mol}$ = 40 g hydrazine
- 2.35 moles ammonia × $17\frac{g}{mol}$ = 39.95 g ammonia

1.9 moles formic acid × $46 \frac{g}{mol}$ = 87.4 g formic acid

5 moles water $\times 18 \frac{g}{mol} = 90 g$ water

0.74 moles ammonia formate × $63 \frac{g}{mol}$ = 46.62 g ammonium formate

(373.5+162) g of reactants - (125+38.7+40+39.95+87.4+90+46.62) g of products = 67.83 g of waste

2. Estimation of energy requirements

The energy requirements for the production of $[P_{66614}][124Triz]$ and all the precursors were estimated using the heat of formation of the reactants and products, according to the following equations²:

$$Q-W = \Delta H + \Delta E k + \Delta E p$$
(S1)

where:

 $\begin{array}{l} \mathsf{Q} = \text{reactor heat consumption} \\ \mathsf{W} = \text{work} \\ \Delta\mathsf{H} = \text{enthalpy of reaction} \\ \Delta\mathsf{E}_{\mathsf{k}} = \text{kinetic energy} \\ \Delta\mathsf{E}_{\mathsf{p}} = \text{potential energy} \end{array}$

$$\Delta H = \sum (n \times \hat{H}) \text{ output streams} - \sum (n \times \hat{H}) \text{ input streams}$$
(S2)

where:

n = molecular weight of reactants \hat{H} = specific enthalpy of reactants

$$\hat{H} = \Delta \hat{H} f^{\circ} + \int_{T1}^{T2} Cp dT$$

where: $\Delta \hat{H} f^{\circ}$ = heat of formation of reactants Cp = calorific value of reactants T1 = reference temperature (25 °C) T2 = temperature of the reactants

The estimated theoretical energy consumption was scaled-up to industrial scale by multiplying it by the correction factors reported in Mehrkesh and Karunanithi³. For heat requirements for endothermic reactions, the estimated theoretical value was converted to the actual heat consumption (assumed to be supplied by natural gas) using a correction factor of 4.2. Similarly, the theoretical heat generated by exothermic reactions was converted to the actual cooling electricity requirements using a correction factor of 3.2.

The physico-chemical properties of the chemicals involved in the synthesis of $[P_{66614}][124Triz]$ and its precursors are summarised in Table S2.

(S3)

2.1 <u>Trihexyl(tetradecyl)phosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz])</u>

The energy inventory for the production of 1000 g of $[P_{66614}][124Triz]$ has been estimated based on the heat requirements of the reactor using eqns. (S1)–(S3). Table S3 shows the input and output streams involved in the synthesis of $[P_{66614}][124Triz]$ based on:

$$1.81 \ C_{38} H_{68} CIP + \bar{R} OH^{-} + 1.81 \ C_{2} H_{3} N_{3} \rightarrow 1.81 \ C_{40} H_{71} PN_{3} + 1.81 \ HCI$$

The specific enthalpies \hat{H} for each chemical compound in the reaction were estimated according to eqn. (3) as follows:

$$\hat{H}1 = \Delta \hat{H}f \circ [P66614]CI (25^{\circ}C) + \int_{25^{\circ}C}^{25^{\circ}C} Cp \ dT = 206.2 \frac{kJ}{mol} + 0 = 206.2 \frac{kJ}{mol}$$
$$\hat{H}2 = \Delta \hat{H}f \circ 1,2,4-\text{triazole} (25^{\circ}C) + \int_{25^{\circ}C}^{25^{\circ}C} Cp \ dT = 108.75 \frac{kJ}{mol} + 0 = 108.75 \frac{kJ}{mol}$$
$$\hat{H}3 = \Delta \hat{H}f \circ [P66614][124\text{Triz}] (25^{\circ}C) + \int_{25^{\circ}C}^{25^{\circ}C} Cp \ dT = 206.2 \frac{kJ}{mol} + 0 = 206.2 \frac{kJ}{mol}$$
$$\hat{H}4 = \Delta \hat{H}f \circ \text{HCl} (25^{\circ}C) + \int_{25^{\circ}C}^{25^{\circ}C} Cp \ dT = -92.31 \frac{kJ}{mol} + 0 = -92.31 \frac{kJ}{mol}$$

The enthalpy of the reaction was calculated using eqn. (S2) based on the specific enthalpy values \hat{H} estimated for each chemical compound involved in the reaction of the synthesis of [P₆₆₆₁₄][124Triz] as shown in Table S4. Hence:

$$\Delta H = \left[\left(1.81 \text{ mol } x \text{ 206.2} \frac{\text{kJ}}{\text{mol}} \right) + \left(1.81 \text{ mol } x \text{ -92.31} \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[\left(1.81 \text{ mol } x \text{ 206.2} \frac{\text{kJ}}{\text{mol}} \right) + \left(1.81 \text{ mol } x \text{ 108.75} \frac{\text{kJ}}{\text{mol}} \right) \right]$$
$$= -363.92 \text{ kJ}$$

According to eqn. (S1), 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. A negative ΔH value indicates that an exothermic reaction is taking place and therefore heat needs to be removed through cooling. Therefore, the theoretical heat needed to be removed from the reactor is equal to:

 $Q \approx \Delta H = -363.92 \text{ kJ} = -0.364 \text{ MJ}$

Using the correction factor 3.2, this heat is equivalent to 1.165 MJ of electricity needed to cool the reactor.

2.2 <u>Trihexyl(tetradecyl)phosphonium hydroxide ([P₆₆₆₁₄][OH])</u>

There is no energy consumption in the production of [P66614][OH] because this is an ionic exchange reaction occurring at room temperature.

2.3 <u>Trihexyl(tetradecyl)phosphonium chloride ([P₆₆₆₁₄]Cl)</u>

The energy requirement for the production of 940 g of $[P_{66614}]CI$ has been estimated based on the heat requirements of the reactor using eqns. (S1)–(S3). Table S4 shows the input and output streams involved in the synthesis of $[P_{66614}]CI$, based on the following reaction:

$$2 \; C_{14} H_{29} CI + 2 \; C_{18} H_{39} P \rightarrow 1.81 \; C_{38} H_{68} CIP + 0.083 \; HCI$$

Chemical compound	Chemical formula	Molecular weight (g/mol)	Calorific value, Cp (kJ/mol K)	Heat of formation, ΔH ^o f 25ºC (kJ/mol)	Assumptions	Source
[P ₆₆₆₁₄][124Triz]	$C_{34}H_{71}PN_{3}$	552	0.772	206.2	ΔHf ^o of ionic liquid [BMIM][DCA] used as proxy	Emel'yanenko et al.4
[P ₆₆₆₁₄]Cl	C ₃₂ H ₆₈ CIP	519	0.772	206.2	ΔHf ^o of ionic liquid [BMIM][DCA] used as proxy	Emel'yanenko et al.4
[P ₆₆₆₁₄][OH]	C ₃₂ H ₆₈ OHP	500				
1,2,4-triazole	$C_2H_3N_3$	69	0.079 ^a	108.75		NIST⁵
1-chlorotetradecane	C ₁₄ H ₂₉ Cl	233	0.5215	-677.04	Extrapolated from ΔHf ^o of 2-chloropropane ^b	Norén and Sunner ⁶
1-hexene	C_6H_{12}	84	0.184	-20.90	ΔH^{o}_{f} of 1-pentene used as proxy	Felder and Rousseau ²
1-tetradecanol	C ₁₄ H ₃₀ O	214	0.516	-484.09		NLM ⁷
Ammonia	NH₃	17	0.044	-67.2		Felder and Rousseau ²
Ammonium formate	NH ₄ HCO ₂	63	0.108	-251	ΔHf ^o of formamide used as proxy	NIST ⁸
Anion exchange resin	ŖΟH ⁻					
Ditetradecyl carbonate	C ₂₉ H ₅₈ O ₃	454				
Ditetradecyl ether	C ₂₈ H ₅₈ O	410				
Formamide	CH₃NO	45	0.108	-251		NIST ⁸
Formic acid	CH_2O_2	46	0.099	-425		NIST ⁹
Hydrazine hydrate	$N_2H_4 \cdot H_2O$	50	0.099	50.48		Green and Perry ¹⁰
Hydrochloric acid	HCI	36	0.0864	-92.31		Felder and Rousseau ²
Methyl ethyl ketone (MEK)	C ₄ H ₈ O	72.1	0.159 ^c	-273.3		NIST ¹¹
Phosgene	COCl ₂	99	0.1088	-220.08		NIST ¹²
Phosphine	PH₃	34	0.037	9.23		Green and Perry ¹⁰
Trihexylphosphine	C ₁₈ H ₃₉ P	287	0.309	82.48	ΔH^{o}_{f} of triphenylphsophine sulfide used as proxy	Kirklin et al. ¹³
Water	H ₂ O	18	0.075	-285.84		Felder and Rousseau ²

Table S2 Physico-chemical properties of chemical compounds used in the synthesis of [P₆₆₆₁₄][124 Triz] and its precursors

^a Cp = 1.14 kJ/kg K ^b Δ Hf^o of 2-chloropropane reported at -144.6 kJ/mol ^c Cp = 2.205 kJ/kg K

Table S3 Input and output streams for the production of [P₆₆₆₁₄][124Triz]

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
C ₃₈ H ₆₈ CIP	1.81	Ĥ1		
$C_2H_3N_3$	1.81	Ĥ2		
$C_{40}H_{71}PN_3$			1.81	Ĥ3
HCI			1.81	Ĥ4

The specific enthalpies \hat{H} for each chemical compound in the reaction were estimated according to eqn. (S3) as follows:

$$\hat{H}1 = \Delta \hat{H}f^{\circ} \text{ trihexylphosphine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp dT} = 82.48 \frac{\text{kJ}}{\text{mol}} + 0 = 82.48 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}2 = \Delta \hat{H}f^{\circ} \text{ 1-chlorotetradecane } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp dT} = -677.04 \frac{\text{kJ}}{\text{mol}} + 0 = -677.04 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}3 = \Delta \hat{H}f^{\circ} \text{ [P66614]Cl } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{140^{\circ}\text{C}} \text{Cp dT} = 206.2 \frac{\text{kJ}}{\text{mol}} + \left(0.772 \frac{\text{kJ}}{\text{mol}} \times 115 \text{ K}\right) = 295.03 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}4 = \Delta \hat{H}f^{\circ} \text{ HCl } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{140^{\circ}\text{C}} \text{Cp dT} = -92.31 \frac{\text{kJ}}{\text{mol}} + \left(0.086 \frac{\text{kJ}}{\text{mol}} \times 115 \text{ K}\right) = -82.37 \frac{\text{kJ}}{\text{mol}}$$

The enthalpy of the reaction was calculated using eqn. (S2) based on the specific enthalpy values \hat{H} estimated for each compound involved in the synthesis of [P₆₆₆₁₄][CI] as shown in Table S4. Thus:

$$\Delta H = \left[1.81 \text{ mol } x \text{ } 295.03 \frac{\text{kJ}}{\text{mol}} + 0.083 \text{ mol } x - 82.37 \frac{\text{kJ}}{\text{mol}} \right] - \left[2 \text{ mol } x \text{ } 82.48 \frac{\text{kJ}}{\text{mol}} + 2 \text{ mol } x - 677.04 \frac{\text{kJ}}{\text{mol}} \right]$$
$$= 1716.28 \text{ kJ}$$

Thus, assuming that no work is carried and that kinetic and potential energy are zero (eqn. (S1)), the total amount of energy needed to heat the reactor is equal to 1.716 MJ.

The actual energy consumption was estimated by multiplying the above amount by a correction factor of 4.2 to convert the theoretical heat to the actual heat, assuming this is provided by natural gas. Therefore, the actual heat needed to heat the reactor is equal to 7.21 MJ.

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
C ₁₈ H ₃₉ P	2	Ĥ1		
C ₁₄ H ₂₉ Cl	2	Ĥ2		
C ₃₈ H ₆₈ CIP			1.81	Ĥ3
HCI			0.083	Ĥ4

Table S4 Input and output streams for the production of [P₆₆₆₁₄]CI

2.4 Trihexylphosphine

Table S5 shows the input and output streams involved in the synthesis of trihexylphosphine based on the following reaction:

2.4 PH₃ + 7.2 C₆H₁₂
$$\rightarrow$$
 2 C₁₈H₃₉P + 0.4 PH₃ + 1.2 C₆H₁₂

The specific enthalpies \hat{H} for the compounds involved in the synthesis of trihexylphosphine were estimated according to eqn. (S3):

$$\hat{H}1 = \Delta \hat{H}f^{\circ} \text{ phosphine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp } d\text{T} = 9.23 \frac{\text{kJ}}{\text{mol}} + 0 = 9.23 \frac{\text{kJ}}{\text{mol}}$$
$$\hat{H}2 = \Delta \hat{H}f^{\circ} \text{ hexene } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp } d\text{T} = -20.9 \frac{\text{kJ}}{\text{mol}} + 0 = -20.9 \frac{\text{kJ}}{\text{mol}}$$
$$\hat{H}3 = \Delta \hat{H}f^{\circ} \text{ phosphine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{70^{\circ}\text{C}} \text{Cp } d\text{T} = 9.23 \frac{\text{kJ}}{\text{mol}} + (0.037 \frac{\text{kJ}}{\text{mol}} \text{x} 45 \text{ K}) = 10.88 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}4 = \Delta \hat{H}f^{\circ} \text{ hexene } (25^{\circ}C) + \int_{25^{\circ}C}^{70^{\circ}C} Cp \ dT = -20.9 \frac{kJ}{mol} + (0.184 \frac{kJ}{mol \ K} \times 45 \ K) = -12.62 \frac{kJ}{mol}$$
$$\hat{H}5 = \Delta \hat{H}f^{\circ} \text{ trihexylphosphine } (25^{\circ}C) + \int_{25^{\circ}C}^{70^{\circ}C} Cp \ dT = 82.48 \frac{kJ}{mol} + (0.309 \frac{kJ}{mol \ K} \times 45 \ K) = 96.4 \frac{kJ}{mol}$$

The enthalpy of the reaction, calculated using eqn. (S2) is thus equal to:

$$\Delta H = \left[0.4 \text{ mol } x \text{ } 10.88 \frac{\text{kJ}}{\text{mol}} + 1.2 \text{ mol } x (-12.62 \frac{\text{kJ}}{\text{mol}}) + 2 \text{ mol } x \text{ } 96.4 \frac{\text{kJ}}{\text{mol}} \right] - \left[2.4 \text{ mol } x \text{ } 9.23 \frac{\text{kJ}}{\text{mol}} + 7.2 \text{ mol } x (-20.9 \frac{\text{kJ}}{\text{mol}}) \right] = 310.39 \text{ kJ}$$

Therefore, making the same assumptions in eqn. (S1) as for the previous precursors, the total theoretical heat needed to heat the reactor is equal to 0.31 MJ. Applying the correction factor of 4.2, the actual heat needed to heat the reactor using natural gas is estimated at 1.3 MJ.

Table S5 Input and output streams for the production of trihexylphosphine

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
PH ₃	2.4	Ĥ1	0.4	Ĥ3
$C_{6}H_{12}$	7.2	Ĥ2	1.2	Ĥ4
C ₁₈ H ₃₉ P			2	Ĥ5

2.5 <u>1-Chlorotetradecane</u>

The energy inventory for the production of 582.5 g of 1-chlorotetradecane has been estimated based on the heat requirements of the reactor using eqns. (S1)–(S3). Table S6 and Table S7 list the input and output streams involved in the first and second steps of the synthesis, respectively, as shown below:

- i) 2.2 $C_{14}H_{30}O$ + 1.5 HCl \rightarrow 1.5 $C_{14}H_{29}Cl$ + 0.6 $C_{14}H_{30}O$ + 0.04 $C_{28}H_{58}O$ + 1.7 H_2O
- ii) 1.5 $C_{14}H_{29}CI + 0.6 C_{14}H_{30}O + 0.04 C_{28}H_{58}O + 1.1 COCI_2 \rightarrow 2 C_{14}H_{29}CI + 0.04 C_{28}H_{58}O + 0.07 C_{29}H_{58}O_3 + 0.7 HCI + 0.6 COCI_2$

Table S6 Input and output streams in reaction i) of the production of 1-chlorotetradecane

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
C ₁₄ H ₃₀ O	2.2	Ĥ1	0.6	Ĥ3
HCI	1.5	Ĥ2	0	
C ₁₄ H ₂₉ Cl			1.5	Ĥ4
H ₂ O			1.7	Ĥ5

Table S7 Input and output streams in reaction ii) of the production of 1-chlorotetradecane

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
C ₁₄ H ₃₀ O	0.6	Ĥ1	0	
C ₁₄ H ₂₉ Cl	1.5	Ĥ2	2	Ĥ4
COCl ₂	1.1	Ĥ3	0.6	Ĥ5
HCI			0.70	Ĥ6

i) As it can be seen in Table S6, the production of ditetradecyl ether is not included in the theoretical energy calculations because it is produced in very small quantities and

physico-chemical data were not available. The specific enthalpies \hat{H} for each chemical species in the reaction i) were estimated according to eqn. (S3) as follows:

$$\hat{H}1 = \Delta \hat{H}f \circ 1 \text{-tetradecanol} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp dT} = -484.09 \frac{\text{kJ}}{\text{mol}} + 0 = -484.09 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}2 = \Delta \hat{H}f \circ \text{HCI} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp dT} = -92.31 \frac{\text{kJ}}{\text{mol}} + 0 = -92.31 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}3 = \Delta \hat{H}f \circ 1 \text{-tetradecanol} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{140^{\circ}\text{C}} \text{Cp dT} = -484.09 \frac{\text{kJ}}{\text{mol}} + \left(0.516 \frac{\text{kJ}}{\text{mol}} \times 115 \text{ K}\right) = -424.75 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}4 = \Delta \hat{H}f \circ 1 \text{-chlorotetradecane} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{140^{\circ}\text{C}} \text{Cp dT} = -677.04 \frac{\text{kJ}}{\text{mol}} + \left(0.5215 \frac{\text{kJ}}{\text{mol}} \times 115 \text{ K}\right) = -617.07 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}5 = \Delta \hat{H}f \circ \text{water} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{140^{\circ}\text{C}} \text{Cp dT} = -285.84 \frac{\text{kJ}}{\text{mol}} + \left(0.0754 \frac{\text{kJ}}{\text{mol}} \times 115 \text{ K}\right) = -277.17 \frac{\text{kJ}}{\text{mol}}$$

Therefore, the total enthalpy for reaction i) is equal to:

$$\Delta H = \left[0.6 \text{ mol } x \left(-424.75 \frac{\text{kJ}}{\text{mol}} \right) + 1.5 \text{ mol } x \left(-617.07 \frac{\text{kJ}}{\text{mol}} \right) + 1.7 \text{ mol } x \left(-277.17 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2.2 \text{ mol } x \left(-484.09 \frac{\text{kJ}}{\text{mol}} \right) + 1.5 \text{ mol } x \left(-92.31 \frac{\text{kJ}}{\text{mol}} \right) \right] = -448.18 \text{ kJ}$$

Making the same assumptions as for the other precursors, the total theoretical cooling energy is equal to 0.448 MJ so that the actual electricity demand for cooling is estimated at 1.43 MJ.

 ii) Ditetradecyl ether and ditetradecyl carbonate are not included in the theoretical energy calculations (see Table S7) because they are produced in very small quantities and their physico-chemical properties data were not available. The specific enthalpies were estimated as follows:

$$\hat{H}1 = \Delta \hat{H}f^{\circ} 1 - \text{tetradecanol} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{80^{\circ}\text{C}} \text{Cp dT} = -484.09 \frac{\text{kJ}}{\text{mol}} + \left(0.516 \frac{\text{kJ}}{\text{mol} \text{K}} \times 55 \text{ K}\right) = -455.71 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}2 = \Delta \hat{H}f^{\circ} 1 - \text{chlorotetradecane} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{80^{\circ}\text{C}} \text{Cp dT} = -677.04 \frac{\text{kJ}}{\text{mol}} + \left(0.521 \frac{\text{kJ}}{\text{mol} \text{K}} \times 55 \text{ K}\right) = -648.34 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}3 = \Delta \hat{H}f^{\circ} \text{ phosgene} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{80^{\circ}\text{C}} \text{Cp dT} = -220.08 \frac{\text{kJ}}{\text{mol}} + \left(0.1088 \frac{\text{kJ}}{\text{mol} \text{K}} \times 55 \text{ K}\right) = -214.09 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}4 = \Delta \hat{H}f^{\circ} 1 - \text{chlorotetradecane} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{120^{\circ}\text{C}} \text{Cp dT} = -677.04 \frac{\text{kJ}}{\text{mol}} + \left(0.5215 \frac{\text{kJ}}{\text{mol} \text{K}} \times 95 \text{ K}\right) = -627.50 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}5 = \Delta \hat{H}f^{\circ} \text{ phosgene} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{120^{\circ}\text{C}} \text{Cp dT} = -220.08 \frac{\text{kJ}}{\text{mol}} + \left(0.1088 \frac{\text{kJ}}{\text{mol} \text{K}} \times 95 \text{ K}\right) = -209.74 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}6 = \Delta \hat{H}f^{\circ} \text{ HCl} (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{120^{\circ}\text{C}} \text{Cp dT} = -92.31 \frac{\text{kJ}}{\text{mol}} + \left(0.0864 \frac{\text{kJ}}{\text{mol} \text{K}} \times 95 \text{ K}\right) = -84.10 \frac{\text{kJ}}{\text{mol}}$$

The total enthalpy for reaction ii) is then equal to:

$$\Delta H = \left[2 \text{ mol } x (-627.50 \frac{\text{kJ}}{\text{mol}}) + 0.6 \text{ mol } x (-209.74 \frac{\text{kJ}}{\text{mol}}) + 0.7 \text{ mol } x (-84.10 \frac{\text{kJ}}{\text{mol}})\right] - \left[0.6 \text{ mol } x (-455.71 \frac{\text{kJ}}{\text{mol}}) + 1.5 \text{ mol } x (-648.35 \frac{\text{kJ}}{\text{mol}}) + 1.1 \text{ mol } x (-214.09 \frac{\text{kJ}}{\text{mol}})\right] = 41.8 \text{ kJ}$$

Assuming that this equal to the total theoretical heat requirement, the actual heat needed to heat the reactor by heat from natural gas is estimated at 0.175 MJ.

2.6 <u>1,2,4-Triazole</u>

The input and output streams involved in the synthesis of 1,2,4-triazole are summarised in Table S8. The synthesis is carried out according to:

 $8.3~CH_3NO$ + $3.24~N_2H_4 \cdot H_2O \rightarrow 1.81~C_2H_3N_3$ + $0.86~CH_3NO$ + $1.25~N_2H_4$ + $2.35~NH_3$ + $1.9~CH_2O_2$ + $5~H_2O$ + $0.74~NH_4HCO_2$ + waste

The specific enthalpies were estimated as follows:

$$\begin{aligned} \hat{H}1 &= \Delta \hat{H}f^{\circ} \text{ formamide } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp } d\text{T} &= -251 \frac{\text{kJ}}{\text{mol}} + 0 = -251 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}2 &= \Delta \hat{H}f^{\circ} \text{ hydrazine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp } d\text{T} = 50.48 \frac{\text{kJ}}{\text{mol}} + 0 = 50.48 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}3 &= \Delta \hat{H}f^{\circ} \text{ water } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} \text{Cp } d\text{T} = -285.84 \frac{\text{kJ}}{\text{mol}} + 0 = -285.84 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}4 &= \Delta \hat{H}f^{\circ} \text{ formamide } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -251 \frac{\text{kJ}}{\text{mol}} + \left(0.108 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -235.4 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}5 &= \Delta \hat{H}f^{\circ} \text{ hydrazine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = 50.48 \frac{\text{kJ}}{\text{mol}} + \left(0.099 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -235.4 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}6 &= \Delta \hat{H}f^{\circ} \text{ hydrazine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = 50.48 \frac{\text{kJ}}{\text{mol}} + \left(0.075 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -274.9 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}7 &= \Delta \hat{H}f^{\circ} \text{ hydrazine } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -285.84 \frac{\text{kJ}}{\text{mol}} + \left(0.079 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -274.9 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}7 &= \Delta \hat{H}f^{\circ} \text{ 1,2,4-\text{triazole } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -251 \frac{\text{kJ}}{\text{mol}} + \left(0.079 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -235.4 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}8 &= \Delta \hat{H}f^{\circ} \text{ ammonium formate } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -251 \frac{\text{kJ}}{\text{mol}} + \left(0.108 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -235.4 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}9 &= \Delta \hat{H}f^{\circ} \text{ formic acid } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -251 \frac{\text{kJ}}{\text{mol}} + \left(0.099 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -410.6 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}10 &= \Delta \hat{H}f^{\circ} \text{ ammonia } (25^{\circ}\text{C}) + \int_{25^{\circ}\text{C}}^{170^{\circ}\text{C}} \text{Cp } d\text{T} = -67.2 \frac{\text{kJ}}{\text{mol}} + \left(0.044 \frac{\text{kJ}}{\text{mol}\text{K}} \times 145 \text{ K}\right) = -60.8 \frac{\text{kJ}}{\text{mol}} \\ \hat{H}10 &= \Delta \hat{H}f^{\circ} \text{ ammonia } (25^{\circ}\text{C}) + \int_{25^{\circ}$$

The total enthalpy is equal to:

 $\Delta H = \left[0.86 \text{ moles } x (-235.4 \frac{\text{kJ}}{\text{mol}}) + 1.25 \text{ moles } x 64.8 \frac{\text{kJ}}{\text{mol}} + 5 \text{ moles } x (-274.9 \frac{\text{kJ}}{\text{mol}}) + 1.81 \text{ moles } x 1239 \frac{\text{kJ}}{\text{mol}} + 2.35 \text{ moles } x (-60.8 \frac{\text{kJ}}{\text{mol}}) + 1.9 \text{ moles } x (-410.6 \frac{\text{kJ}}{\text{mol}}) + 0.74 \text{ moles } x (-235.4 \frac{\text{kJ}}{\text{mol}}) \right] - \left[8.3 \text{ moles } x (-251 \frac{\text{kJ}}{\text{mol}}) + 3.24 \text{ moles } x 50.48 \frac{\text{kJ}}{\text{mol}} + 3.24 \text{ moles } x (-285.84 \frac{\text{kJ}}{\text{mol}}) \right] = 1569.9 \text{ kJ}$

Table S8 Input and output streams for the production of 1,2,4-triazole

Chemical compound	n input (mol)	Ĥ input (kJ/mol)	n output (mol)	Ĥ output (kJ/mol)
CH₃NO	8.30	Ĥ1	0.86	Ĥ4
N_2H_4	3.24	Ĥ2	1.25	Ĥ5
H ₂ O	3.24	Ĥ3	5.00	Ĥ6
$C_2H_3N_3$			1.81	Ĥ7
NH ₄ HCO ₂			2.35	Ĥ8
CH ₂ O ₂			1.90	Ĥ9
NH_3			0.74	Ĥ10

Thus, the theoretical energy is equal to 1.57 MJ and the actual heat requirement using natural gas is estimated at 6.59 MJ.

A second reactor is needed in the synthesis of 1,2,4-triazole to separate the product from impurities using MEK as an extraction solvent. The mixture is heated from 80 °C to 100 °C and the theoretical heating requirements were calculated using the heat transfer equation:

 $Q = m \times Cp \times \Delta T$

where: Q = heat m = mass of the reactant Cp = calorific value of reactant $\Delta T = temperature differential$

Hence:

0.125 kg of 1,2,4-triazole × 1.14 $\frac{kJ}{kg K}$ × (100 °C-80 °C)= 2.84 kJ 0.557 kg of MEK × 2.205 $\frac{kJ}{kg K}$ ×(100 °C-80 °C)=24.57 kJ

Therefore, the theoretical heat needed to heat the 1,2,4-triazole and MEK mixture is equal to 0.0274 MJ. Using a correction factor of 4.2, the actual heat supplied by natural gas is estimated at 0.115 MJ.

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