Supplementary Information:

Improved rare earth elements recycling using a sustainable diglycolamide-based hydrophobic eutectic solvent

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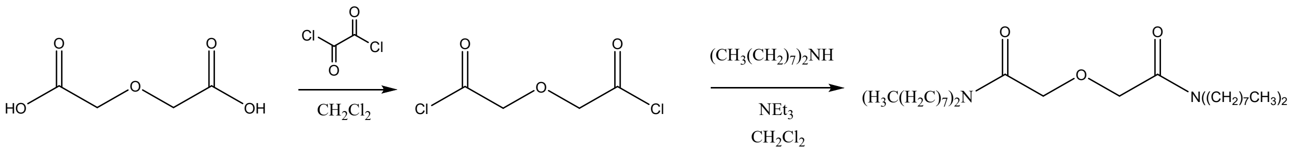
I. Synthesis of TODGA:



Diglycolic acid was reacted with oxalyl chloride in dichloromethane in the presence of a small amount of dimethylformamide, which acted as an initiator for its conversion into the corresponding acid chloride. This acid chloride was then reacted with dioctylamine in dichloromethane containing triethylamine. The product was extracted and concentrated, then the resulting residue was purified after being solubilized in ethyl acetate and filtered through silica. This provided *N*,*N* ,*N*',*N*'-tetraoctyl-3-oxapentanediamide (TODGA) with a purity of over 95%.

II. Extraction data:

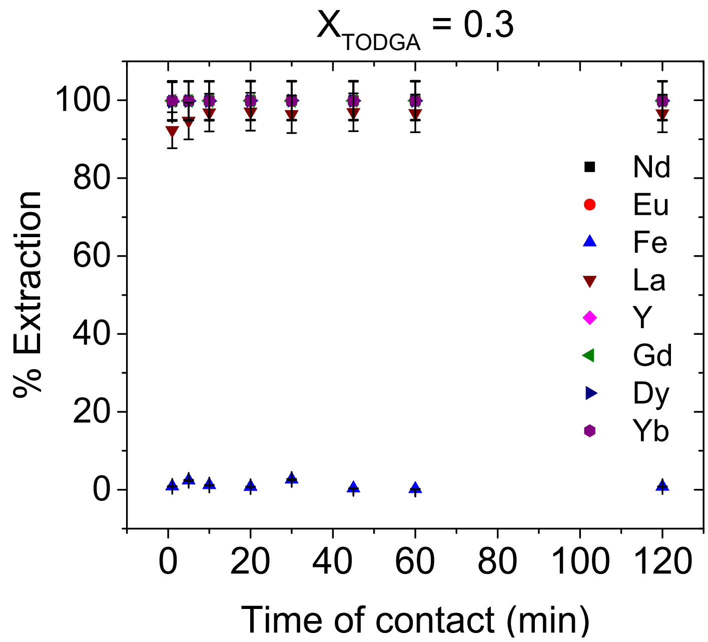


Figure S1: Extraction percentage of Nd, Eu, Fe,Y,Gd,Dy,Yb,La for the TODGA/DA (x_{TODGA} = 0.3) as a function of the contact time

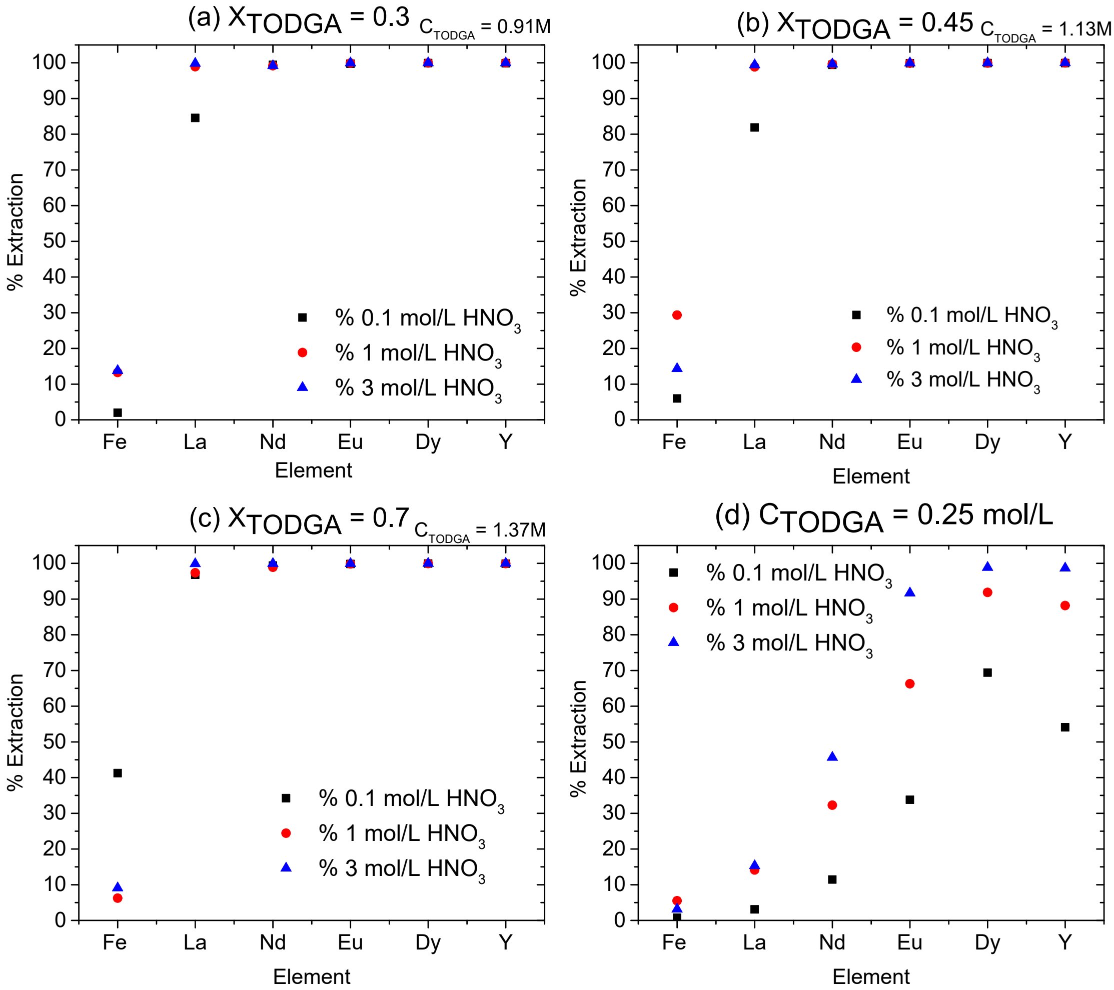


Figure S2: Extraction efficiency (in percentage) of lanthanides and iron ions in the TODGA/DA systems at 0.1, 1.0, and 3.0 mol/L of HNO_3 for different organic phases: (a) x_{TODGA}= 0.3 ([TODGA]= 0.91 mol/L), (b) x_{TODGA}= 0.45 ([TODGA]= 1.13 mol/L), (c) x_{TODGA}= 0.7 ([TODGA]= 1.37 mol/L) and (d) reference system TODGA at 0.25 mol/L in dodecane with 5% volume of octanol.

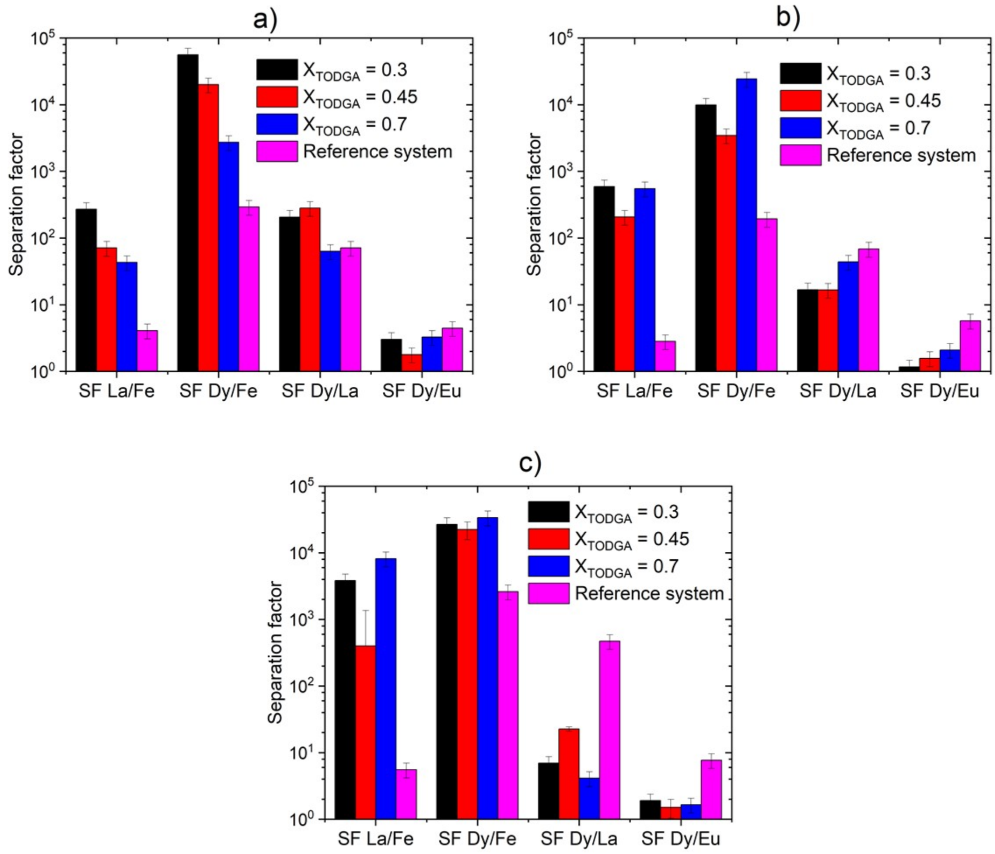


Figure S3: Separation factors obtained for TODGA/DA systems at a) 0.1, b)1.0, and c)3.0 mol/L of HNO_3 for x_{TODGA}=0.3, x_{TODGA}=0.45, x_{TODGA}=0.7 and the reference system TODGA at 0.25 mol/L in dodecane with 5% volume of octanol.

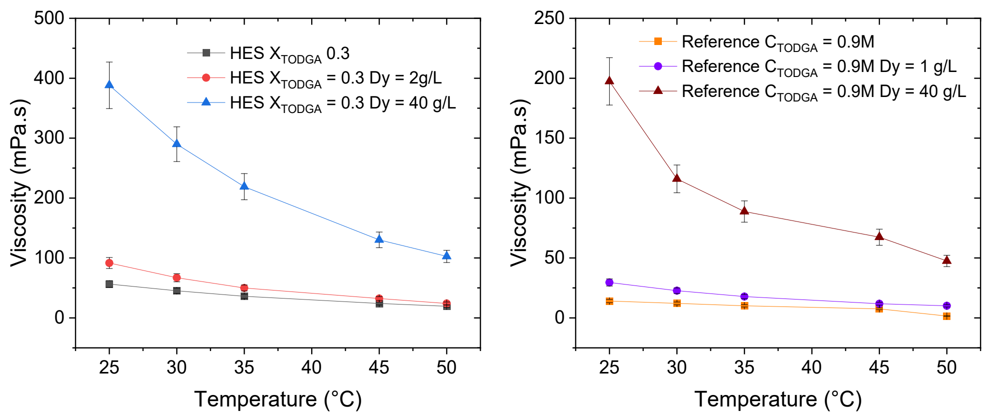
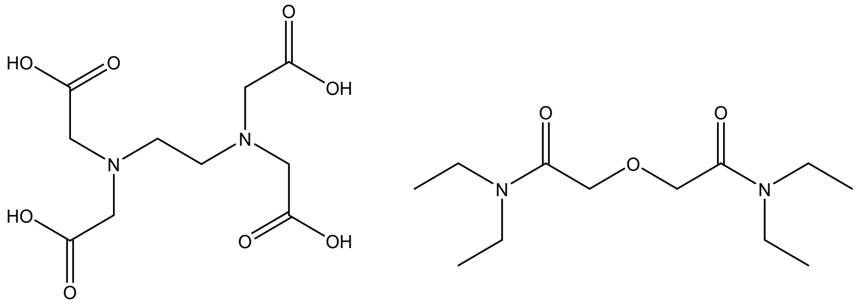


Figure S4: Viscosity of the HES system and the reference system as a function of the temperature and metal loading (before contact and after contact with a 1M HNO_3 containing 1 g/L and 50 g/L Dy, respectively).



Ethylenediaminetetraacetic acid (EDTA)

N,*N*,*N'*,*N'*-Tetraethyl Diglycolamide (TEDGA)

Figure S5: Structure of the aqueous soluble stripping agent studied in this work

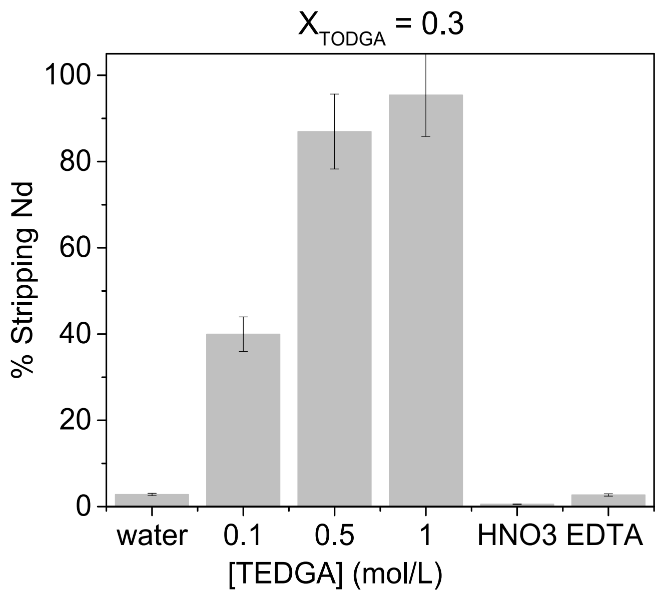


Figure S6: Stripping percentage of Nd after extraction with the TODGA/DA system (x_{TODGA} = 0.3) as a function of the aqueous stripping phase composition (only water, TEDGA, HNO_3 and EDTA).

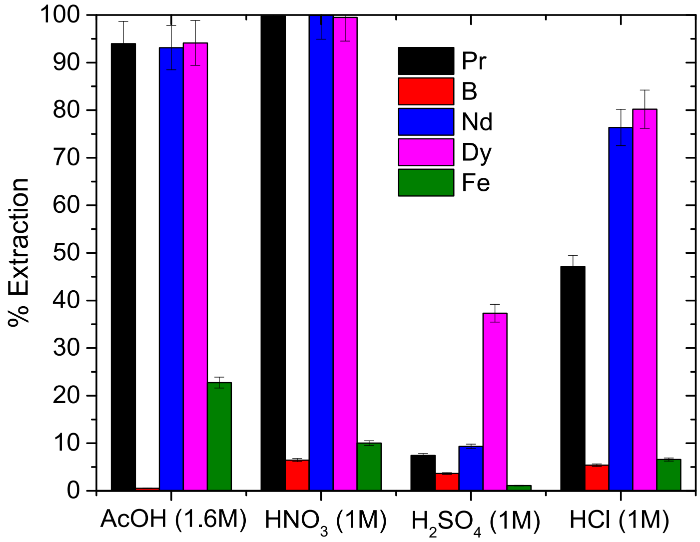


Figure S7 : Extraction efficiency (in percentage) of cations (Pr, B, Nd, Dy, Fe) from various leaching solutions by the HES system with TODGA/DA (x_{TODGA} = 0.3).

III. LCA

Table S1: Inventory data calculated for 1 t of solvent.

Inventory parameters	Unit	Reference solvent: TODGA 0.25M in dodecane octanol (5% v/v)	HES TODGA-DA (x_{TODGA} = 0.3)	HES TODGA-DA (x_{TODGA} = 0.45)	HES TODGA-DA (x_{TODGA} = 0.7)
		Quantity			
Input material					
TODGA	kg	229.8	600.6	747.2	905.0
Octanol	kg	73	0	0	0
Dodecane	kg	1498.4	414.8	270.3	114.8
Energy consumption					
Electricity (centrifugation)	kWh	0	160	160	160
Emissions to air					
VOC	kg	802.1	15.4	17.6	19.8

Table S2: Reagents needed to produce 1 t of TODGA

Reagent	Quantity (kg)
Diglycolic acid	335.0
Oxalyl chloride	1332.5
Dichloromethane	16625.0
Dimethylformamide	47.2
Dioctylamine	1510.0
Triethylamine	630.0
Ethyl acetate	6765.0
HCL 1 mol/L	10000.0
NaCl (saturated)	12000.0

LCA data was calculated with the software SimaPro 9.5.0.2 with the EF 3.1 method, and by using the ecoinvent processes given in the following table for the production of chemicals and electricity. Proxy processes had to be chosen when the exact chemicals were not available. The quantities of input chemical products were estimated by considering one refill of the chemicals after their respective evaporation. Impact of electricity centrifugation has been evaluated by considering Portuguese electricity mix. End-of-life of solvents and leachates were not taken into account in this study, and only one cycle of solvent and evaporation was considered.

Table S3: Ecoinvent processes chosen in the SimaPro software

Input	Ecoinvent process
Diglycolic acid	Diethylene glycol {RER}| ethylene glycols production, thermal hydrolysis of ethylene oxide | Cut-off, U
Oxalyl chloride	Acetyl chloride {RER}| acetyl chloride production | Cut-off, U
Dichloromethane	Dichloromethane {RER}| dichloromethane production | Cut-off, U
Dimethylformamide	N,N-dimethylformamide {RER}| N,N-dimethylformamide production | Cut-off, U
Dioctylamine	Dipropyl amine {RER}| dipropyl amine production | Cut-off, U
Triethylamine	Triethyl amine {RER}| triethyl amine production | Cut-off, U
Ethyl acetate	Ethyl acetate {RER}| ethyl acetate production | Cut-off, U
HCL 1 mol/L	Hydrochloric acid, without water, in 30% solution state {RER}| Mannheim process | Cut-off, U
NaCl (saturated)	Sodium chloride, brine solution {RER}| sodium chloride production, brine solution | Cut-off, U
Octanol	Fatty alcohol {RER}| fatty alcohol production, petrochemical | Cut-off, U
Dodecane	Dodecanol {GLO}| dodecanol production, ziegler process | Cut-off, U
Electricity	Electricity, low voltage {PT}| market for electricity, low voltage | Cut-off, U

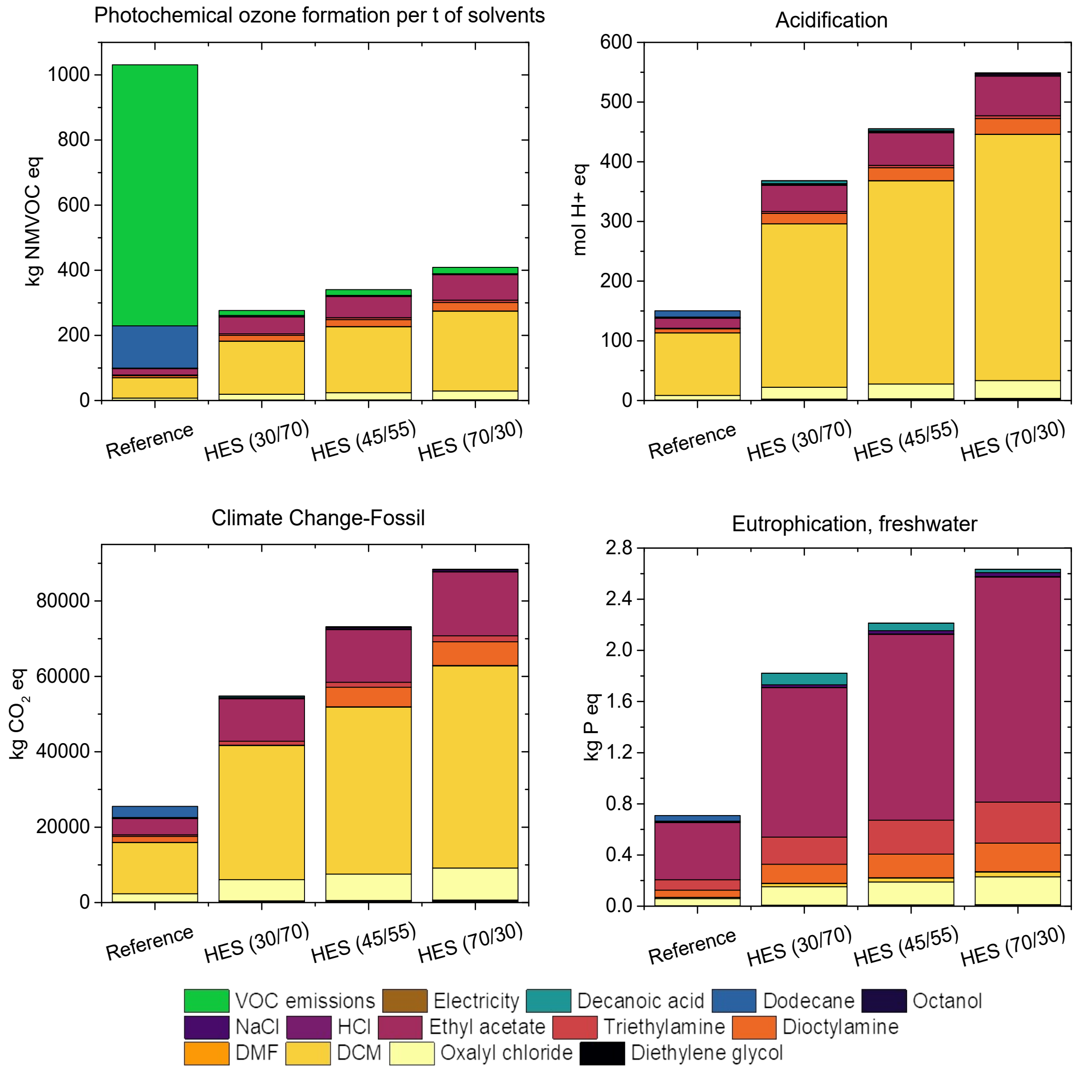


Figure S8: LCA results to produce 1t of solvents

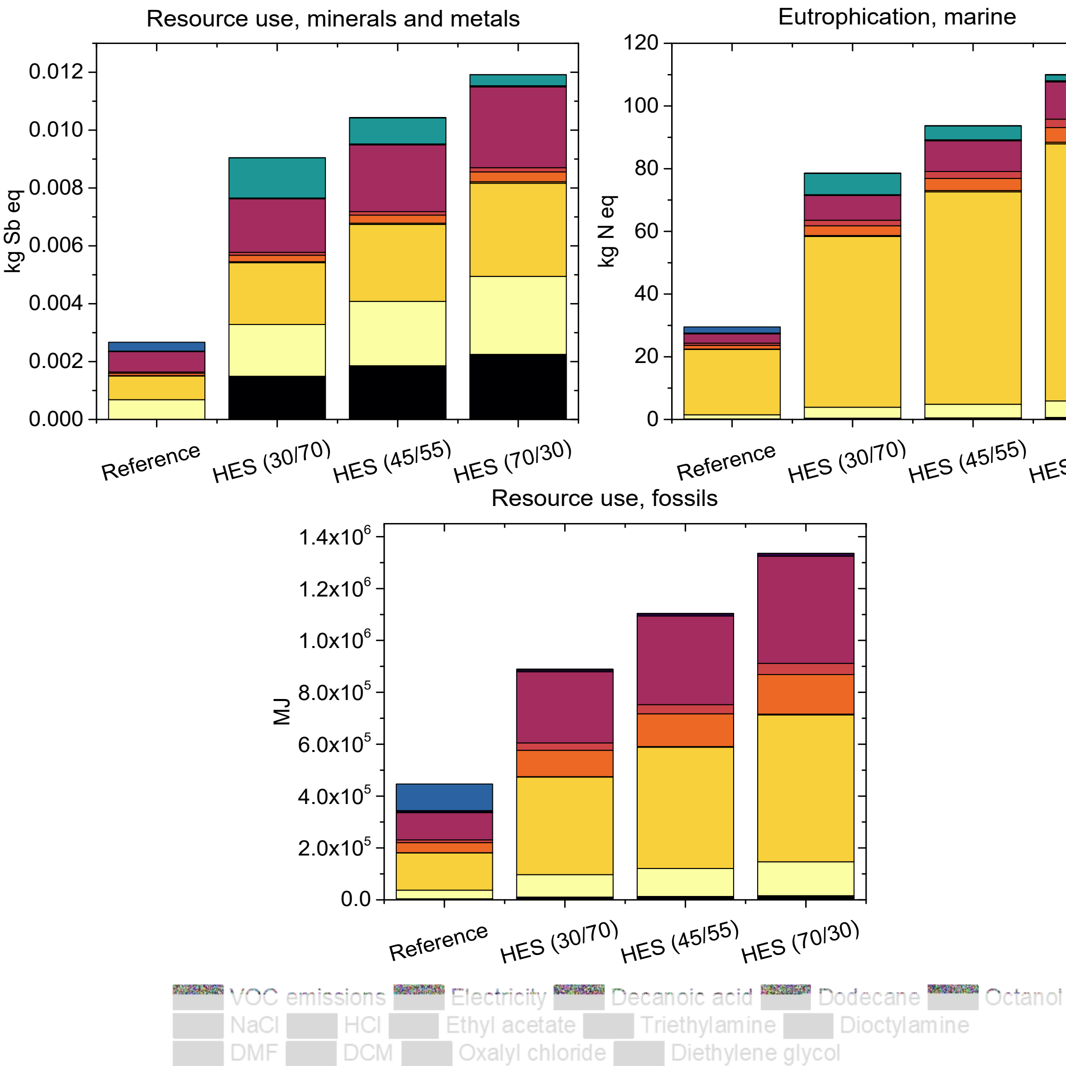


Figure S9: LCA results to produce 1t of solvents

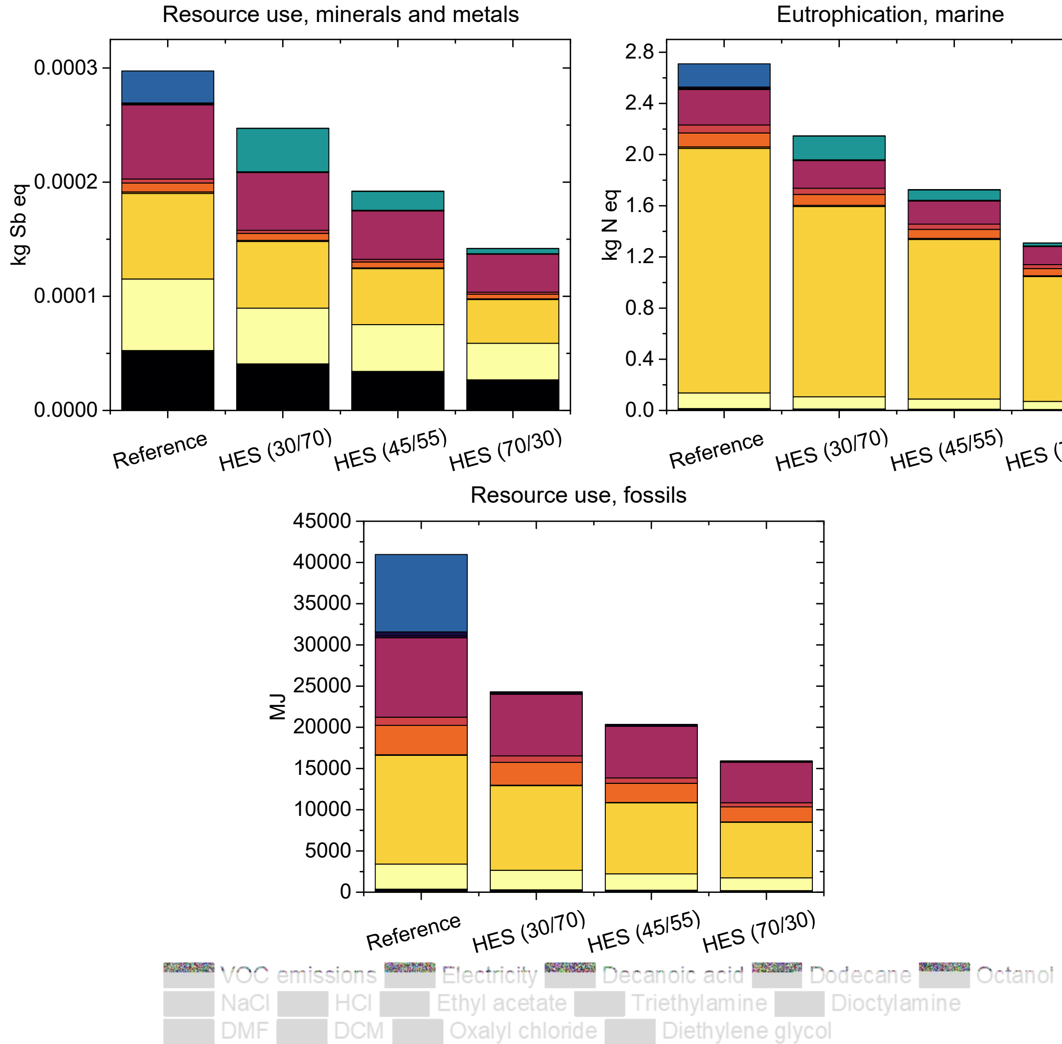


Figure S10: LCA results for 1kg of Dysprosium extracted