Hydrophobic eutectic solvent based on diglycolamide for the recovery of lanthanide elements

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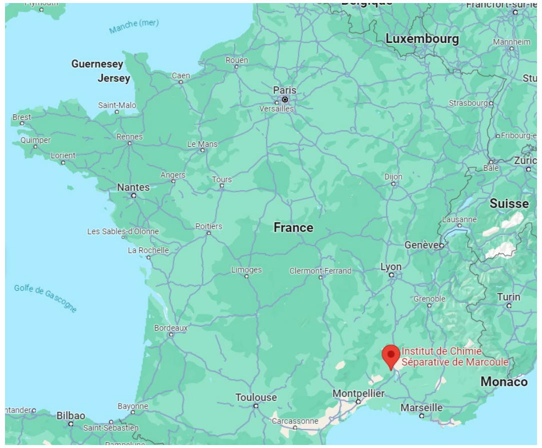

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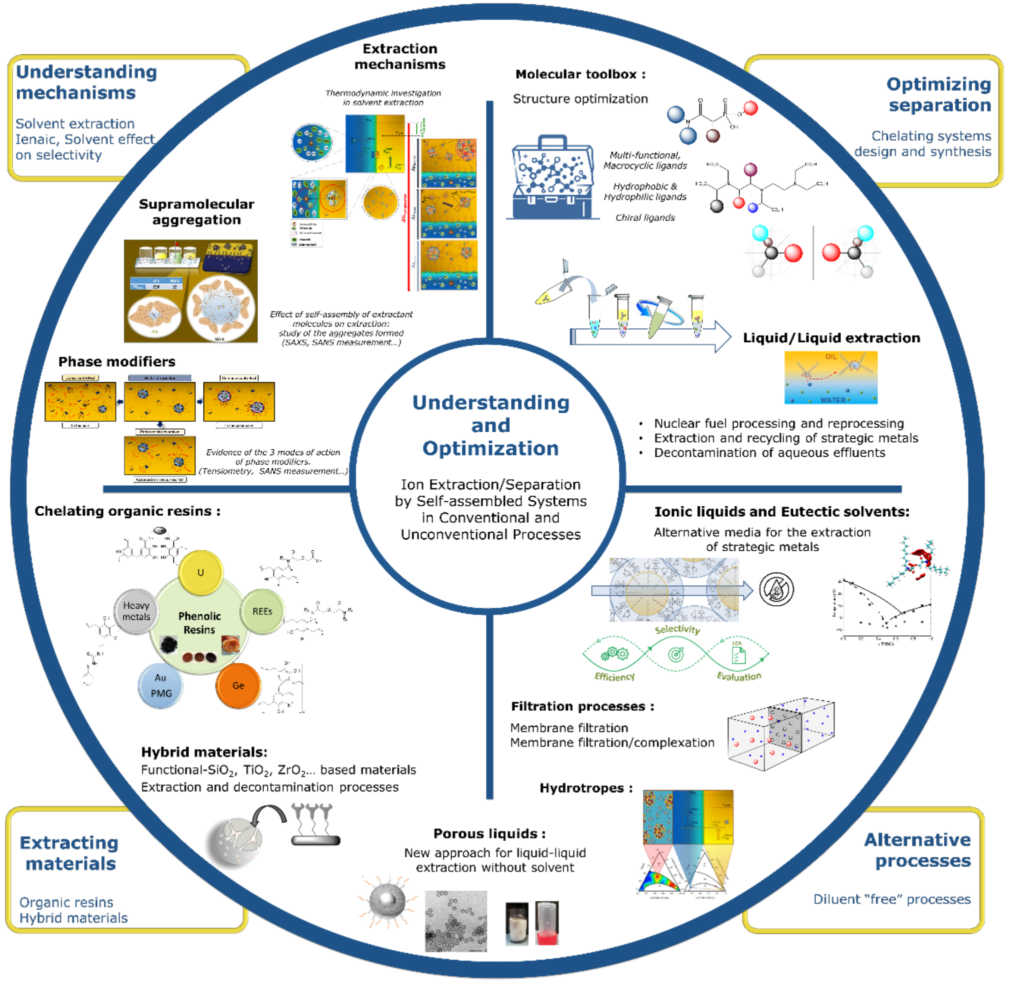
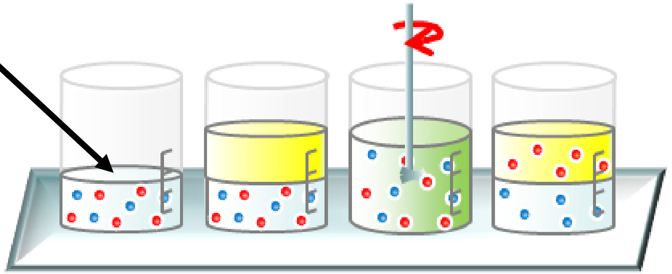


Understanding and optimize hydrometallurgical process

HES to solve problems of Liquid-liquid extraction



- Non selective extraction
- Third phase formation
- Volatile solvents

Alternative to classical solvents

Metals of interest from:
- Ores mining
- Nuclear waste treatment
- Electronic waste recycling, …

The promise of **Hydrophobic Eutectic Solvents**

- Liquids at room temperature,
- Less volatile
- Less toxic
- Often organically sourced

Mixture of hydrogen bond donor (HBD) and acceptor (HBA)

HBA

HBD

MIXING

HES

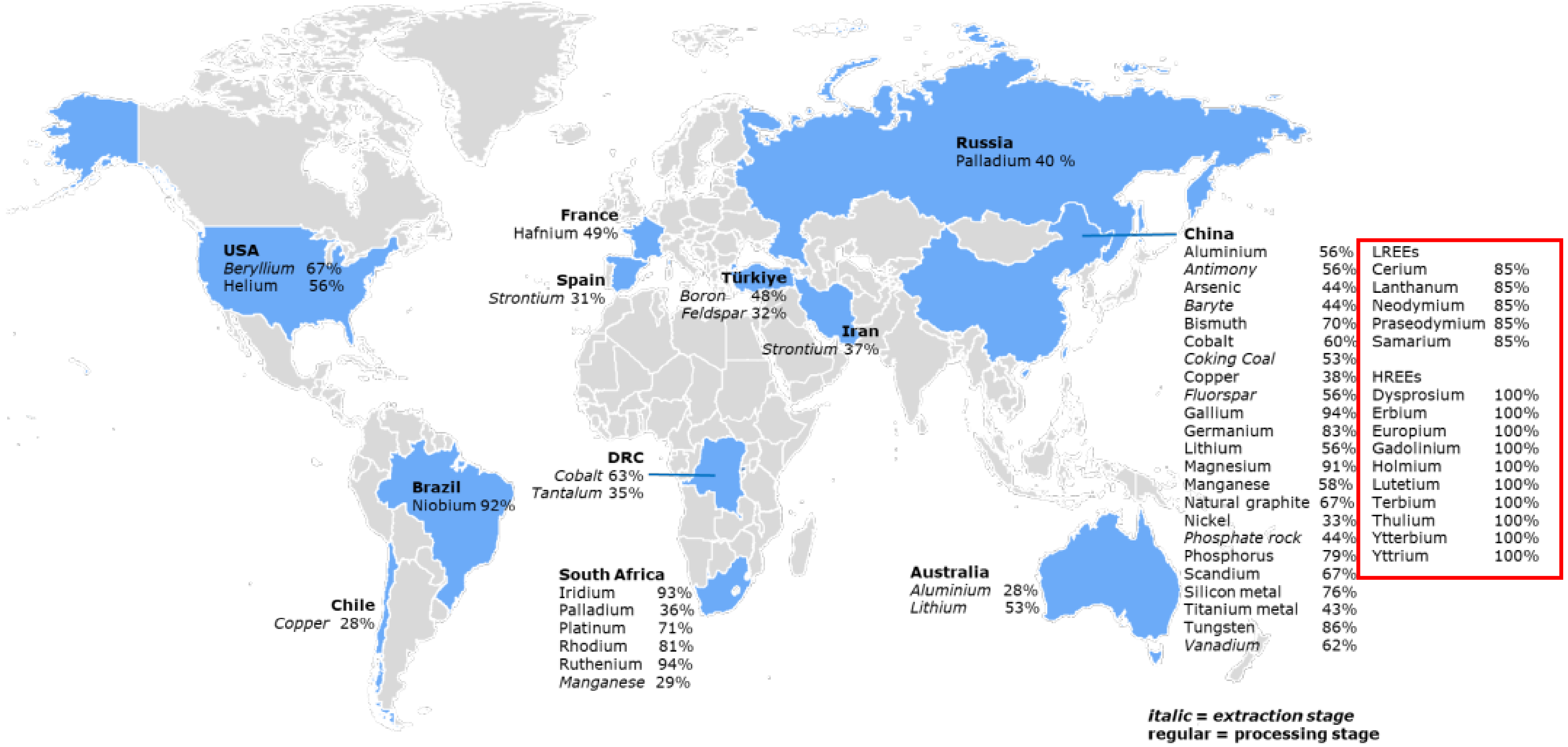
HES as Eco-Friendly Solvents in Extraction Processes

RSC Advances 2021, 11, 31197–31207; Processes 2021, 9, 1202; ACS Sustainable Chemistry & Engineering 2020, 8, 4, 1954-1963; Hydrometallurgy 2019, 189, 105107 ; Separation and Purification Technology 2018, 196, 174-182; Dalton Transactions, 2017, 46, 16505-16515

Rare earth extraction

Critical raw materials in 2011, 2014, 2017, 2020 and 2023		
Antimony	Germanium	Natural graphite
Beryllium	Heavy rare earth elements	Niobium
Cobalt	Indium	PGMs
Fluorspar	Light rare earth elements	Tungsten
Gallium	Magnesium	

Critical raw materials classified by the European Commision

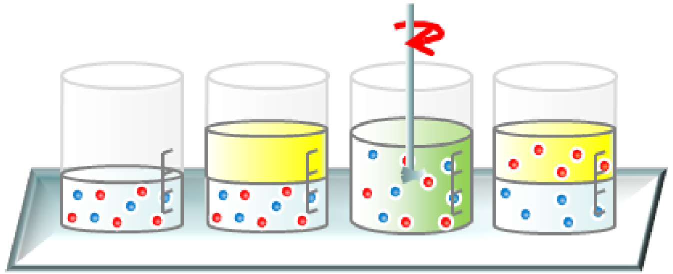


Reference: Study on the Critical Raw Materials for the EU 2023 European Commision.

Design of hydrophobic eutectic solvents (HES) for liquid-liquid extraction of REE

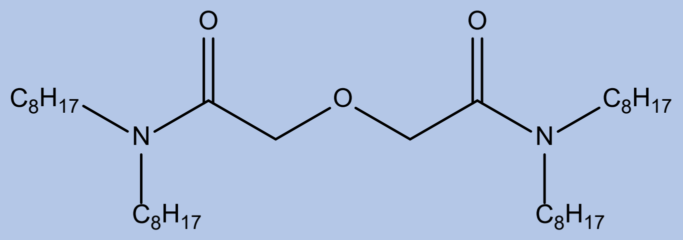
Coll. Aveiro University,
N. Schaeffer, J Coutinho

universidade
de aveiro

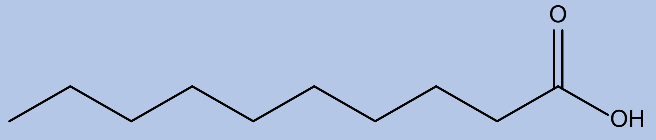


Organic phase = pure HES

HBA = conventional extractant + HBD = fatty acids



N,*N*,*N'*,*N'*- Tetraoctyl Diglycolamide
(*TODGA*)



Decanoic acid
(*DA*)

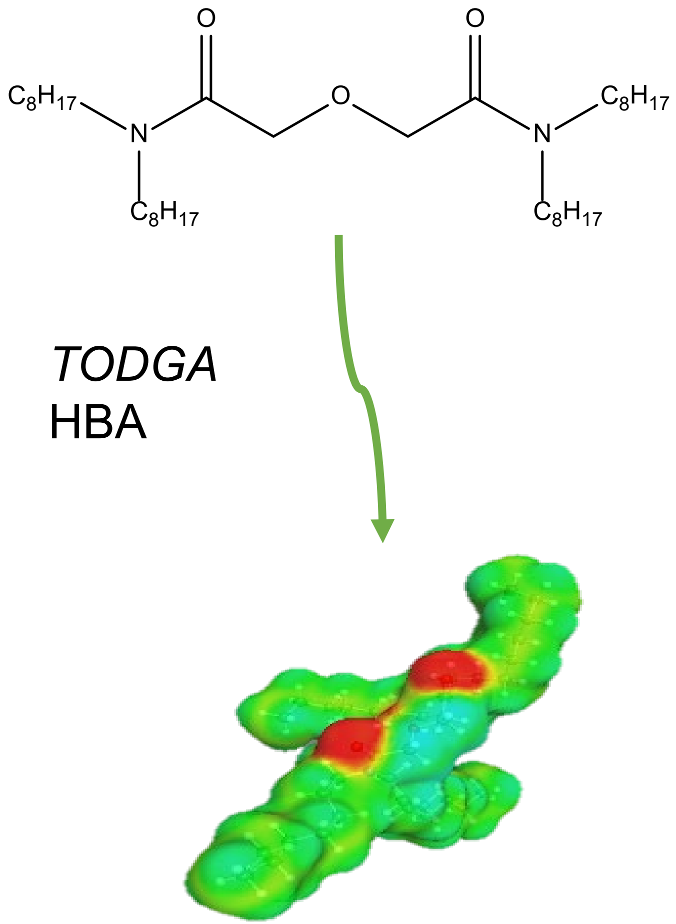
Reference :
TODGA in dodecane and octanol (5%v/v)

Evaluating extraction efficiency

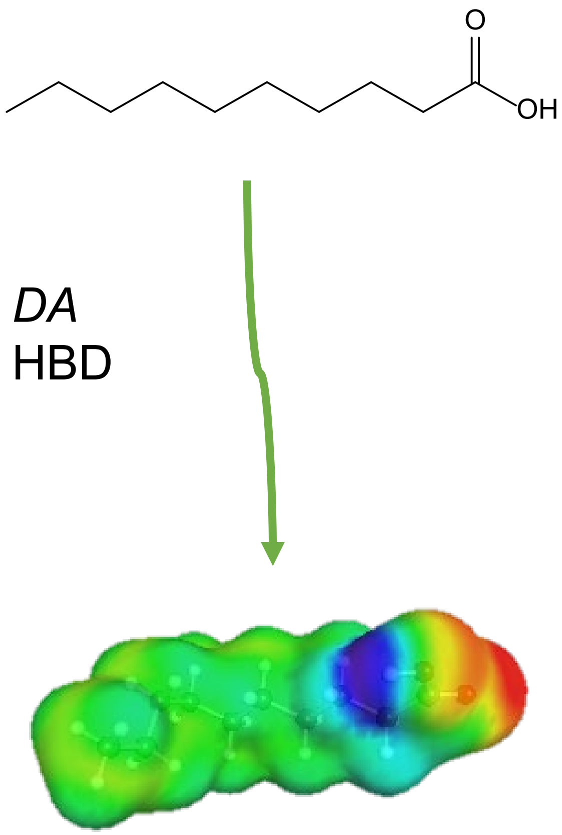
Understanding mechanisms

Formation of a HES: prediction and characterization

Prediction of HES formation by COSMO-RS model

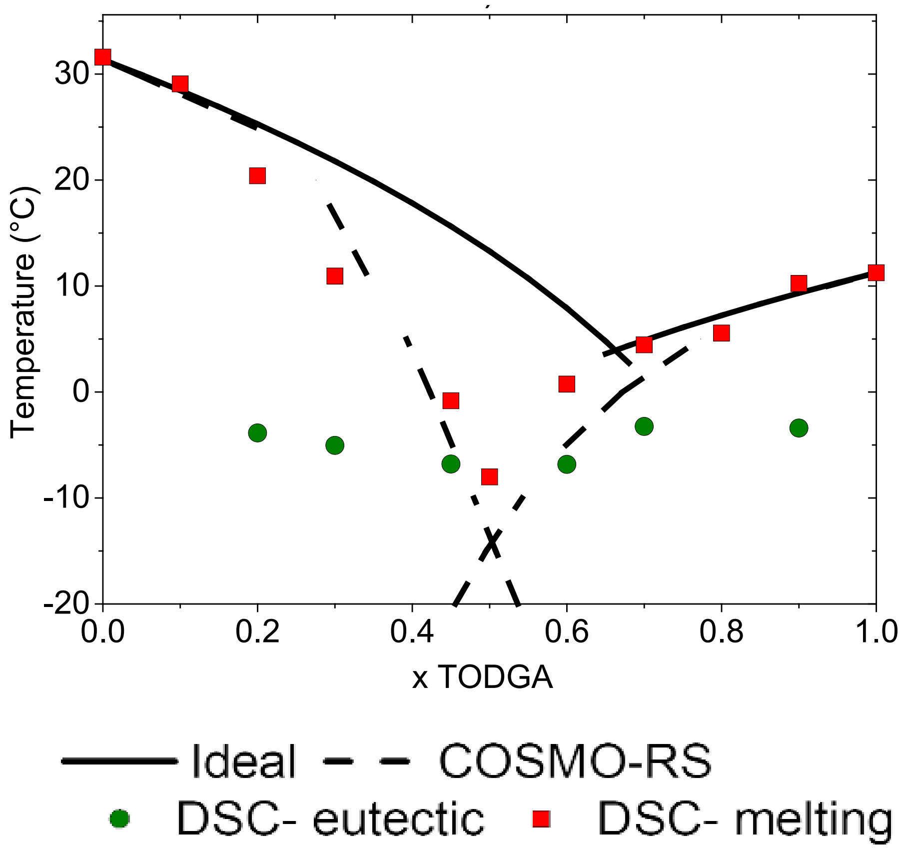


TODGA
HBA



DA
HBD

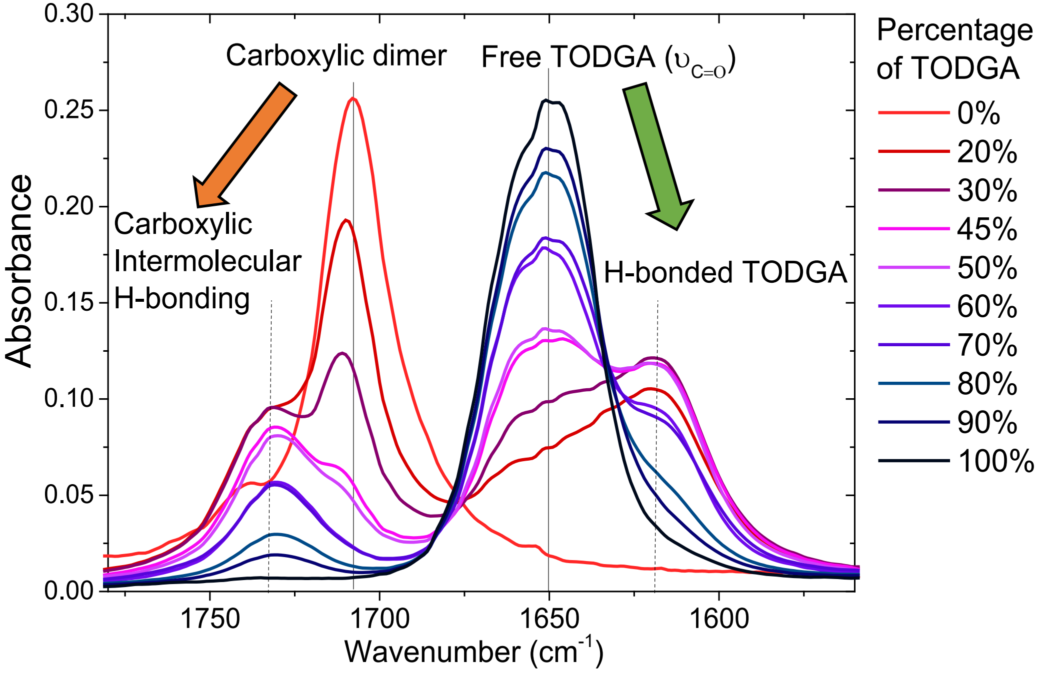
Phase Behavior of HES: Experimental vs Ideal Thermodynamic Profiles



➢ Similarity between COSMO-RS and DSC

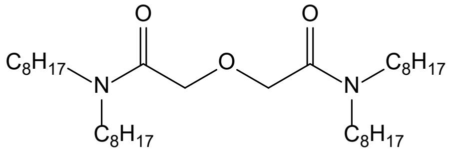
Origin and properties of HES

Structure of H bond network: FTIR

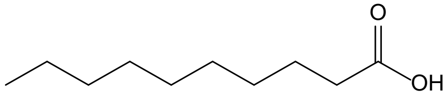


Increase the % of TODGA:

- ➢ Decrease the % of carboxylic dimer
- ➢ Leads to an increase of the H-bonded extractant peak



TODGA



DA

Physico-chemical properties for LLE

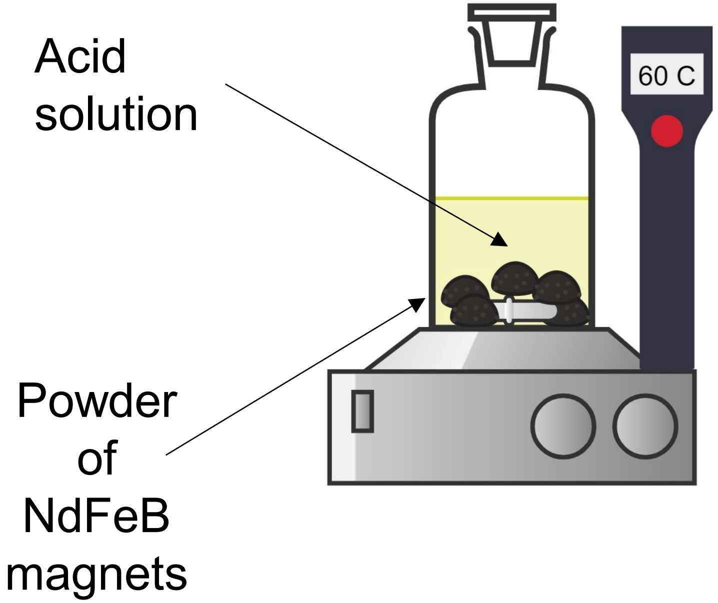
System	Density (g/cm^3)	Viscosity (mPa.s)	% Loss of organic phase	% Water after contact (% wt)
TODGA 0.25 mol/L in dodecane octanol (5% v/v)	0.775	2.29 ± 0.11	0.051	0.31
TODGA DA, x_{TODGA} = 0.30	**0.907**	**58.3 ± 2.9**	**0.016**	**3.22**
TODGA DA, x_{TODGA} = 0.45	0.905	87.7 ± 4.4	0.019	2.69
TODGA DA, x_{TODGA} = 0.70	0.904	120,0 ± 6.0	0.019	2.35

HES system:

- ➢ Loss of organic phase comparable to the reference
- ➢ Density allows phase separation
- ➢ Applicable for Liquid-Liquid extraction

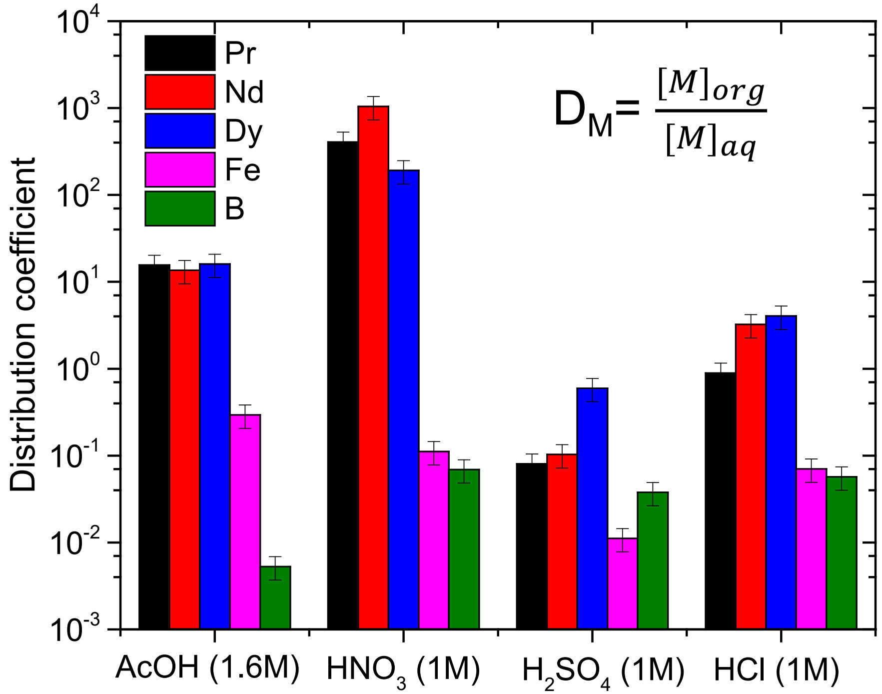
REE extraction using various leaching solutions

Leaching of permanent magnets:
HCl, HNO_3 H_2SO_4 and AcOH



Liquid-liquid extraction of leachate by HES

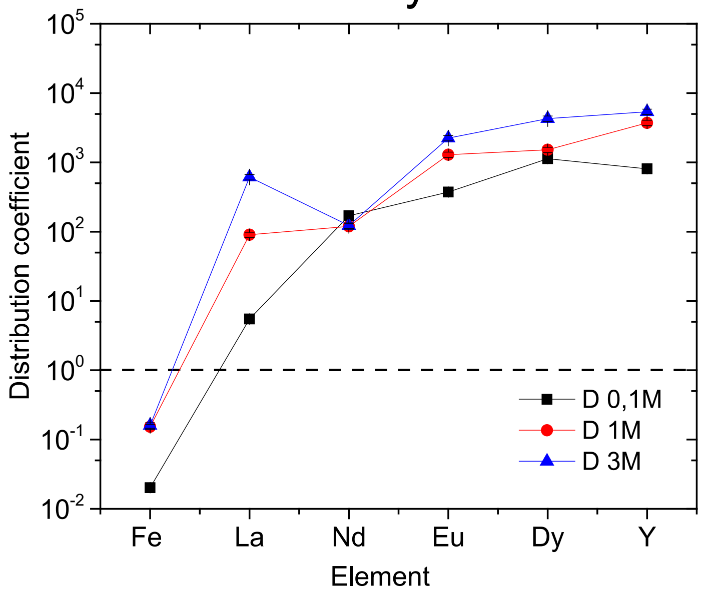
System: TODGA/DA (X_{TODGA} = 0.3)



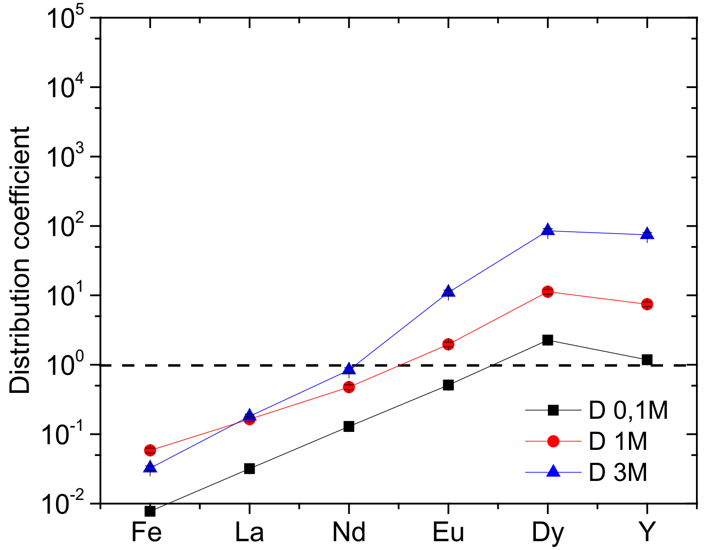
- Significant extraction of Pr, Dy and Nd (D>10) for acetic acid or nitric acid leachate

Selectivity of extraction

HES system



Reference

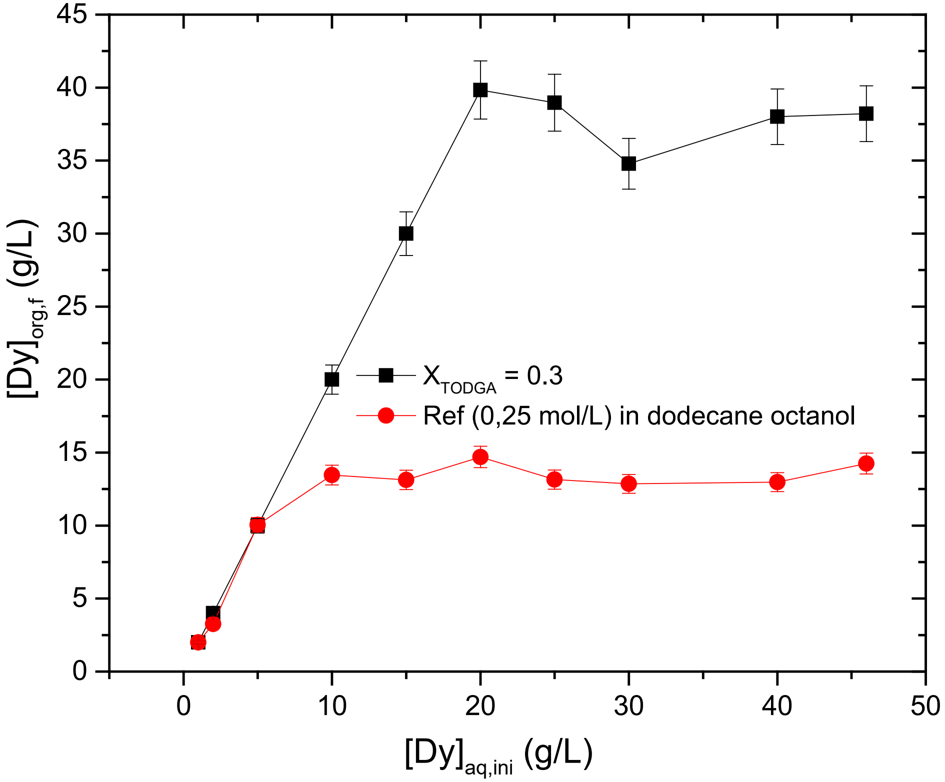


- Extraction of Fe, La, Nd, Eu, Dy, Y at 0.05 M in nitric acid (0.1; 1 and 3 M)

TODGA/DA (X_{TODGA} = 0.3 ; [TODGA] = 0.9M)
vs
Reference TODGA 0.25 M dodecane + 5% octanol

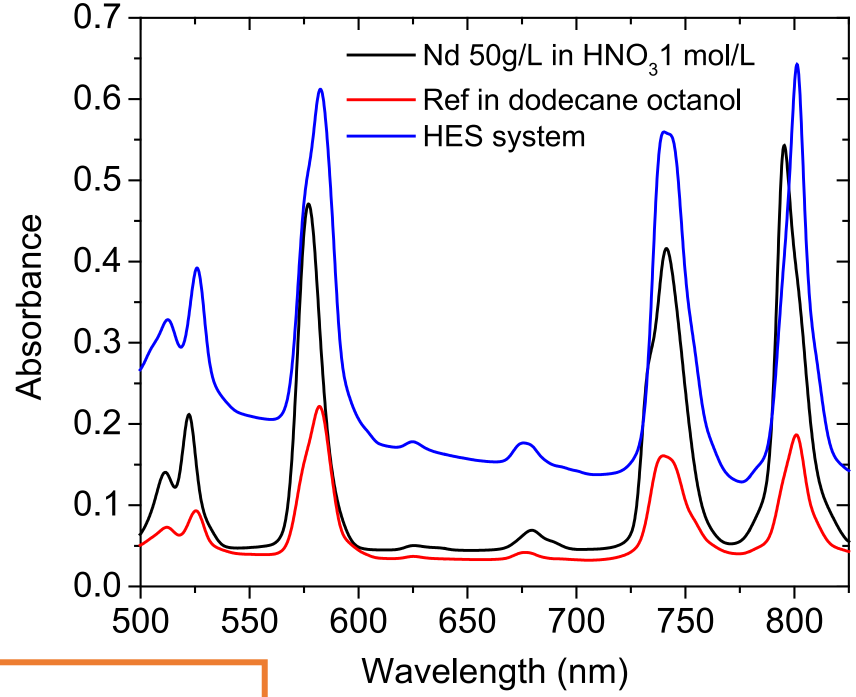
- Reference system exhibit higher intra-lanthanides selectivity
- HES more efficient system with a better selectivity vs iron
- High extraction even at low acidity for HES system

Mechanisms: metal environment in HES

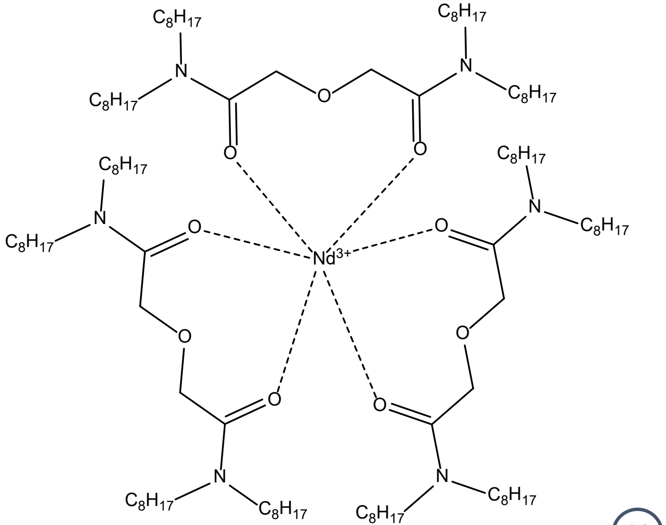


- Loading 3 times higher for the HES than for the conventional solvant capacity

- Uv-vis spectra of Nd



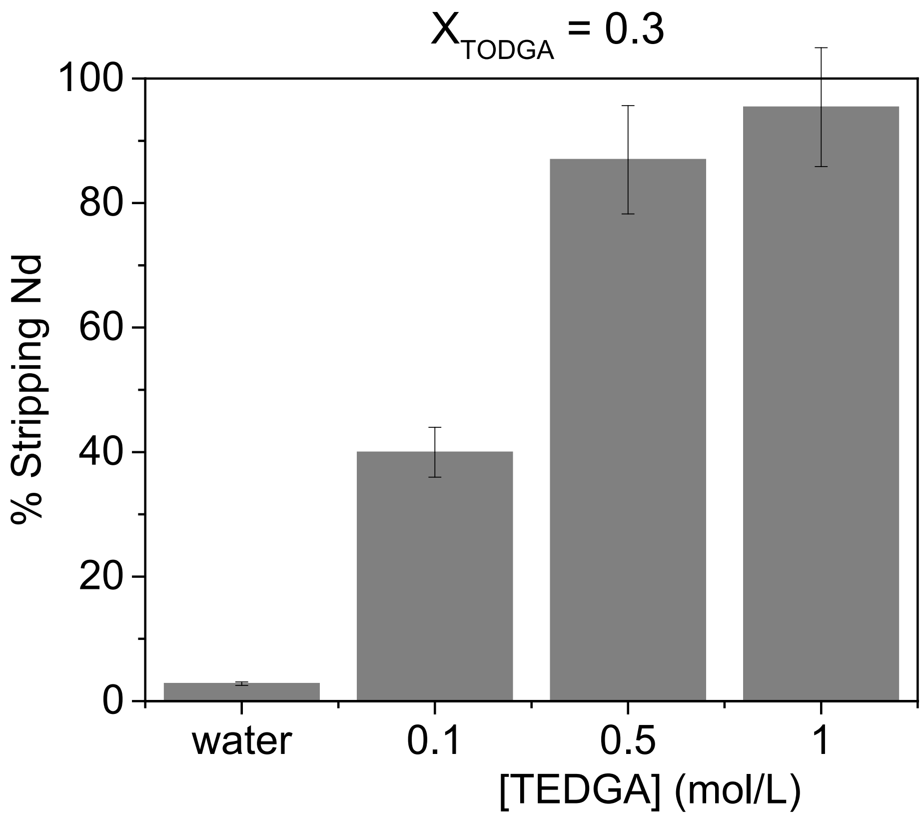
- Difference of environment between aqueous phase and organic phase
- No difference between reference system and HES phase
- Complex Lanthanides-TODGA linked to loading capacity



R. J. Ellis, D. M. Brigham, L. Delmau, A. S. Ivanov, N. J. Williams, M. N. Vo, B. Reinhart, B. A. Moyer and V. S. Bryantsev, *Inorg. Chem.*, 2017, **56**, 1152–1160.

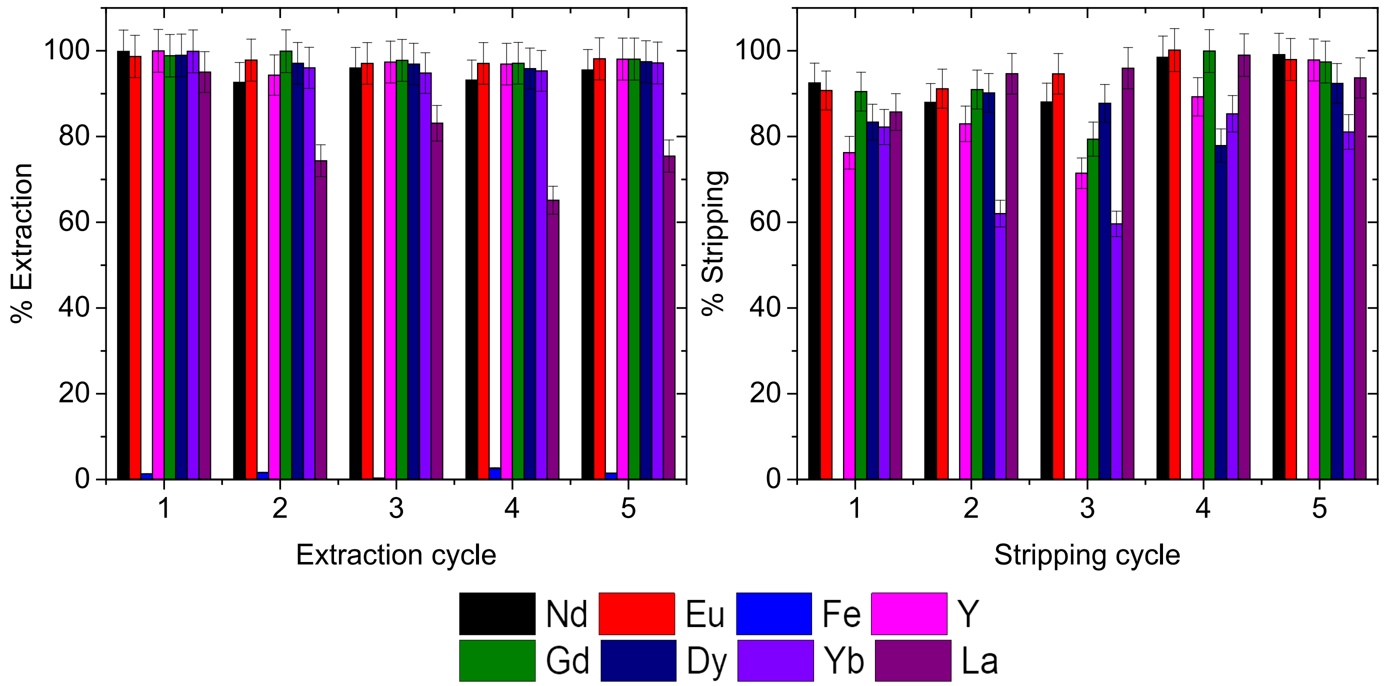
HES recyclability

Influence of stripping agent



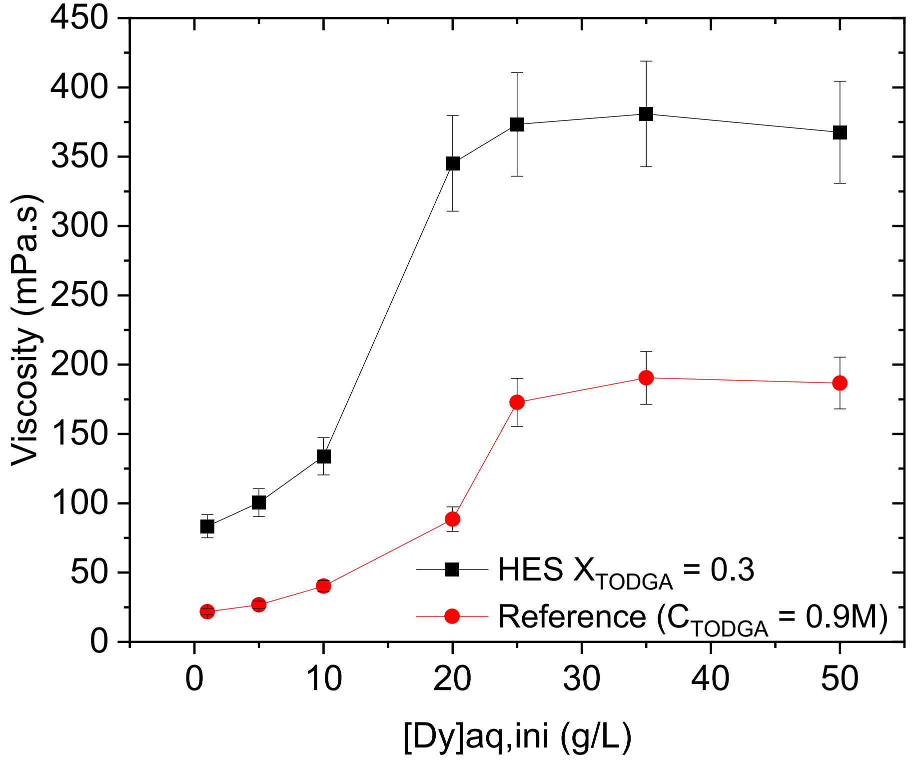
- Quantitative stripping with TEDGA in aqueous phase after contact with a loaded organic HES phase

Five cycles with HES (X_{TODGA}=0.3) as organic phase and TEDGA as stripping agent

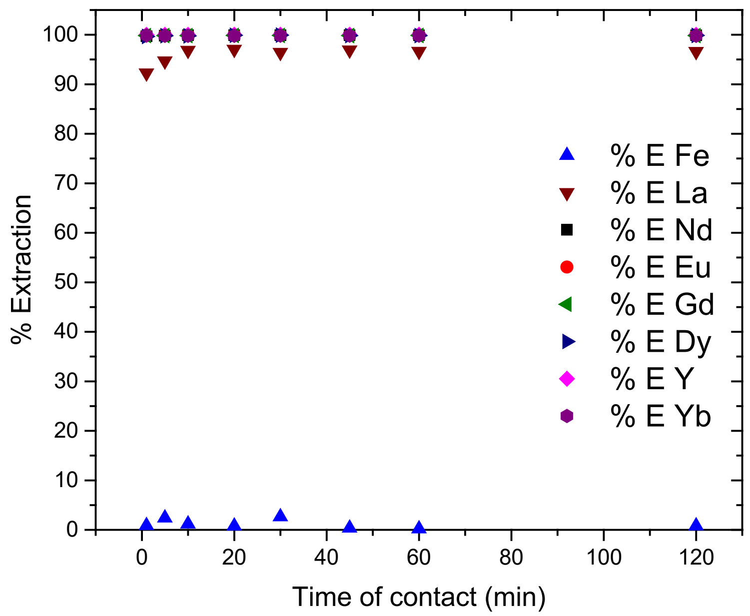


- Loss of stripping capacity after 1 cycle for ytterbium
- But for the other lanthanides stripping stay > 90%

Applicability: Viscosity



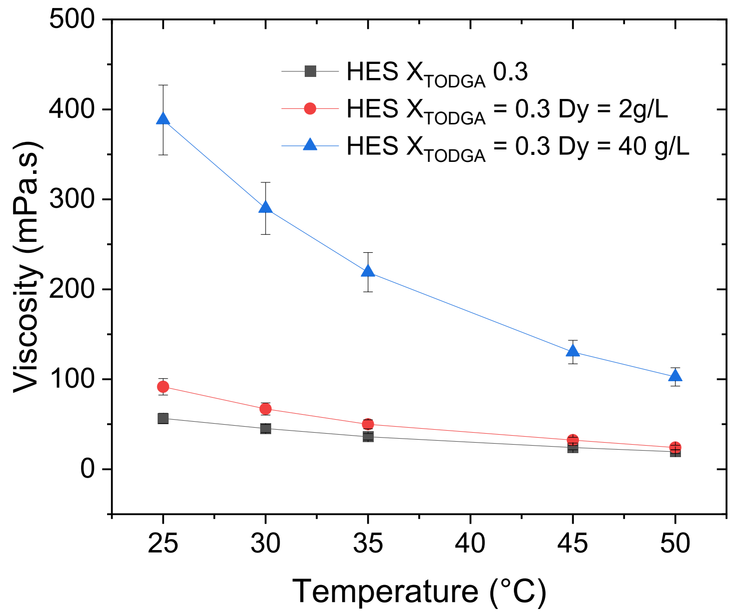
- Fast kinetic
- Kinetic of extraction not affected



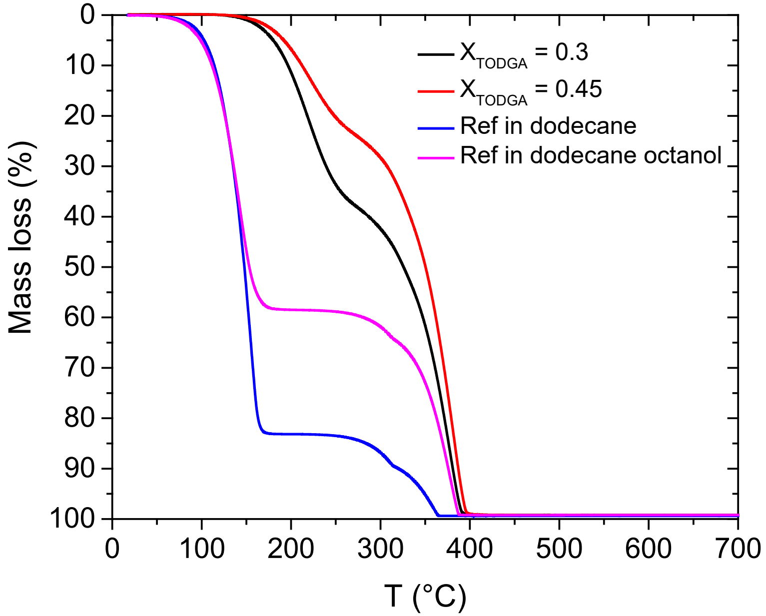
- HES system: more viscous

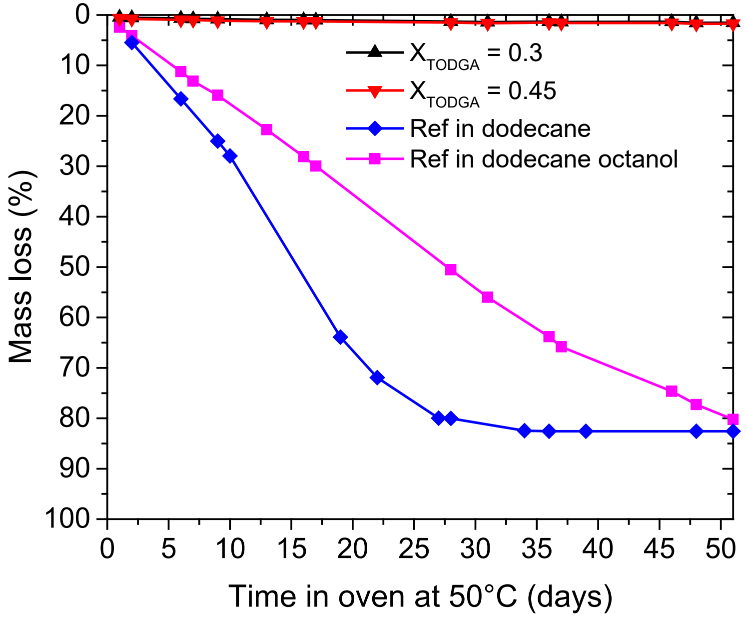
Increase of the viscosity with metal extraction

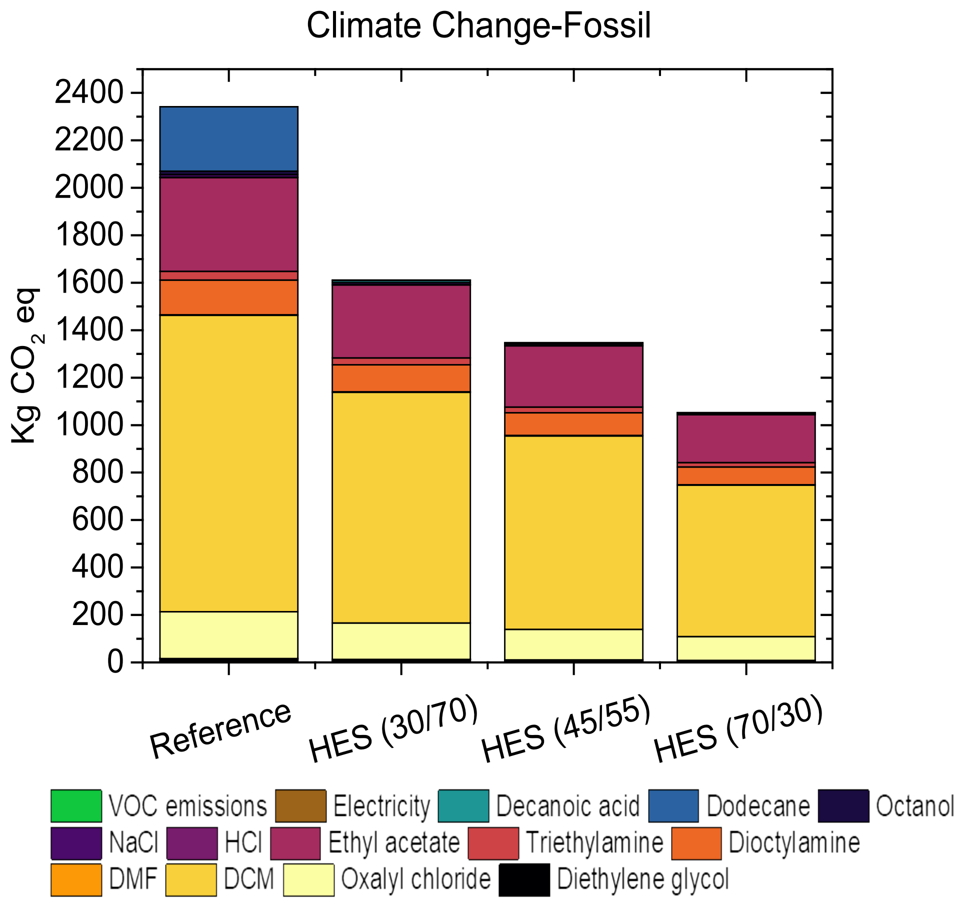
- Decrease of the viscosity with the temperature



Environnemental impact: Comparative LCA HES/Conventional Solvant



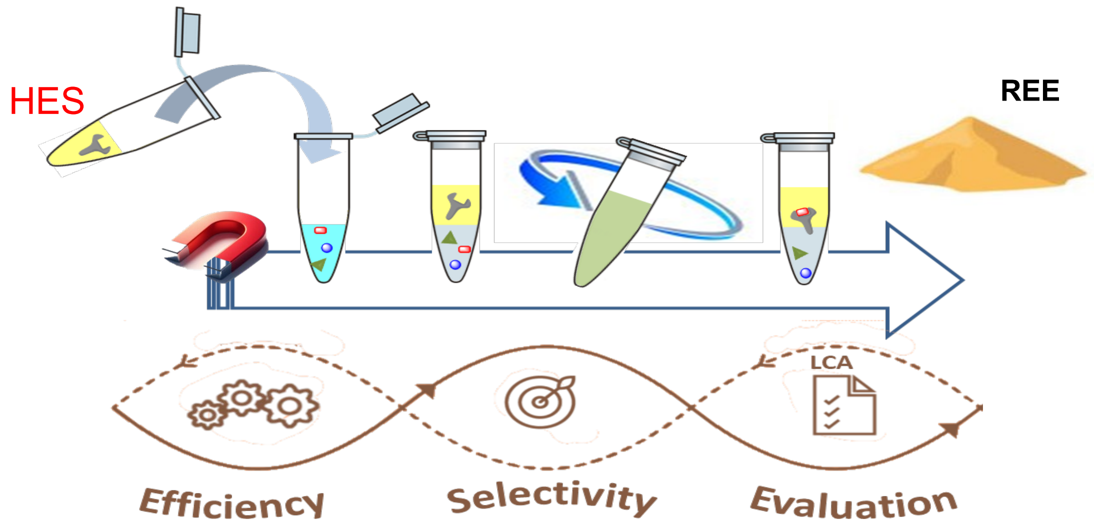




HES: less degradation + less volatile + high extraction
➢ Much lower environnemental impact

Coll. A. Dias

Conclusion and Perspectives



- **HES: Good alternative to classical systems**
- Loading capacity multiplied by 3 – No 3rd phase
- HES viscosity can easily be overcome
- LCA: Lower environmental impact and less volatile system

Further optimization ?

➢ Bio-sourced extractants - lower environmental and economical impact

Acknowledgments

For further informations:

Publications:

- **Design and characterization of novel hydrophobic eutectic solvents based on metal-extracting ligands** : B.Bernicot ;G.Arrachart ;S.Dourdain ;N.Schaeffer ;G.Teixeira ; S.Pellet-Rostaing,https://doi.org/10.1016/j.molliq.2025.127332, Journal of molecular liquids
- **Improved rare earth elements recycling using a sustainable diglycolamide-based hydrophobic eutectic solvent**; B. Bernicot,G. Arrachart, S. Dourdain, N. Schaeffer, Ana C. Dias, S. Pellet-Rostaing, Accepted Green Chemistry

Patents:

- Guilhem Arrachart, Dourdain Sandrine, Pellet-Rostaing Stéphane and Bernicot Baptiste sur l'extraction des terres rares par des solvants eutectiques hydrophobes **n° dépôt FR 2409446 (05/09/2024)**

-**PhD defense**: 7 november
-**Looking for a position**

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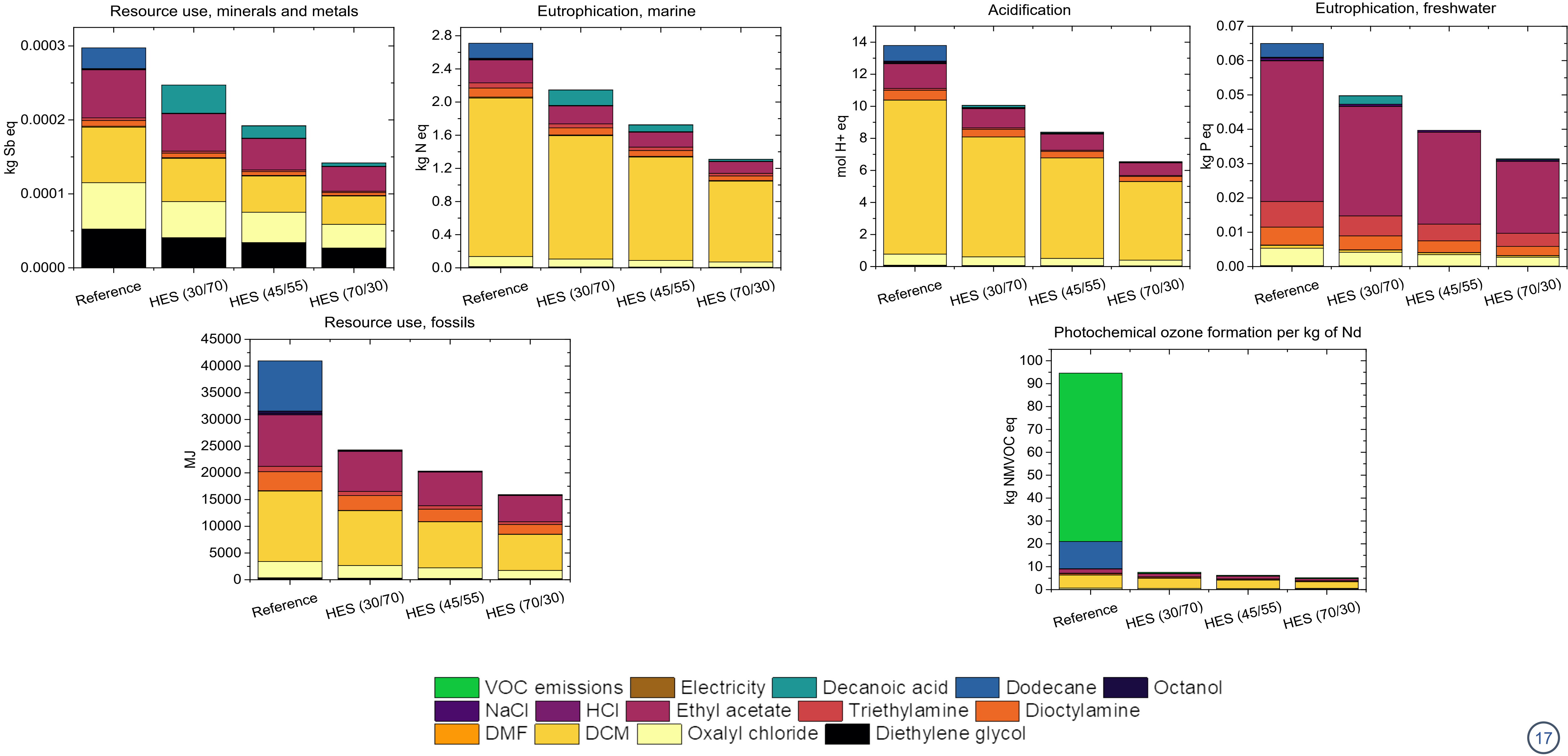
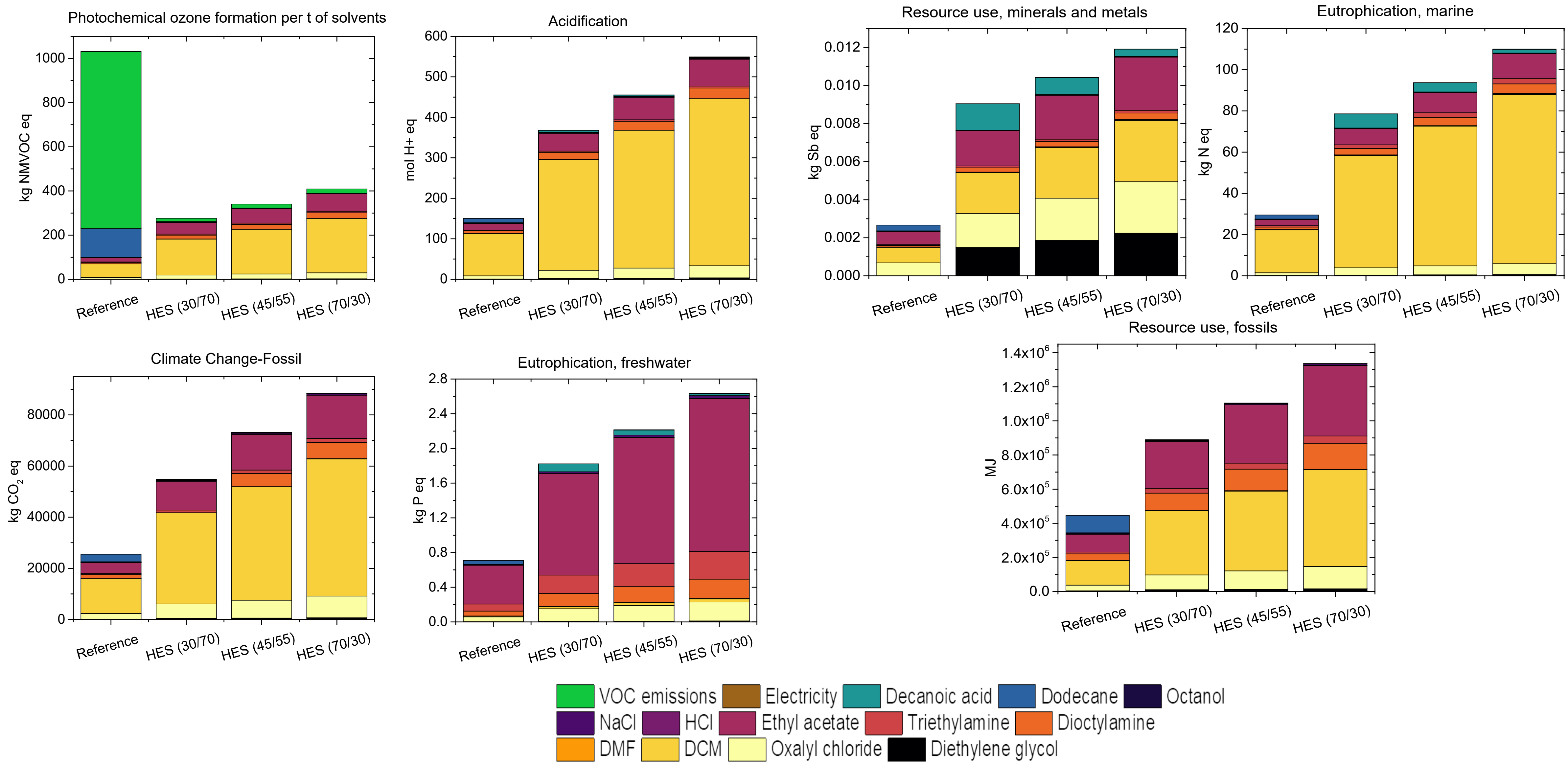
THANK YOU FOR YOUR ATTENTION

LCA for extraction of 1 kg of Nd



LCA to produce 1t of solvents



Inventory

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

Reagents to produce 1t 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

Inventory

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

LCA data 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.