Low temperature solutions for oily soil removal in laundry

Akos Kokai,[••] Kira Lou,[•] Julia Varshavsky,[•] Marley Zalay[•]

University of California, Berkeley
Berkeley Center for Green Chemistry
[•] School of Public Health - Division of Environmental Health Sciences
[••] Environmental Science, Policy & Management - Division of Society & Environment

Presentation roadmap

Challenge
Background
Strategies
- Natural deep eutectic solvents (NADES)
- Biobased solvents
- Biosurfactants
- Enzymes
- Oil-adhesive surfaces

Conclusion

Identify safer, sustainable, and effective new solutions for cleaning oily soils out of clothes in laundry at low temperatures.

Challenge
Background
Strategies
Conclusion


method®
seventh
GENERATION
TM
bioamber™
AMYRIS®

Why is oily soil a problem?
Why low temperatures?

Challenge
Background
Strategies
Conclusion

Removing oily stains requires **energy:** chemical, thermal, and mechanical.

Lower wash temperatures **reduces energy consumption**, one of the biggest life-cycle impacts of laundry.

Design criteria

Be effective in cold water wash (5 - 20 °C).

Prevent redeposition of suspended soils.

Degrade readily.

Have low toxicity (human & ecological).

Prefer renewable feedstocks (bio-based).

Constraints

Focus on liquid laundry detergent products.
(Even though new solutions may have applications beyond these.)

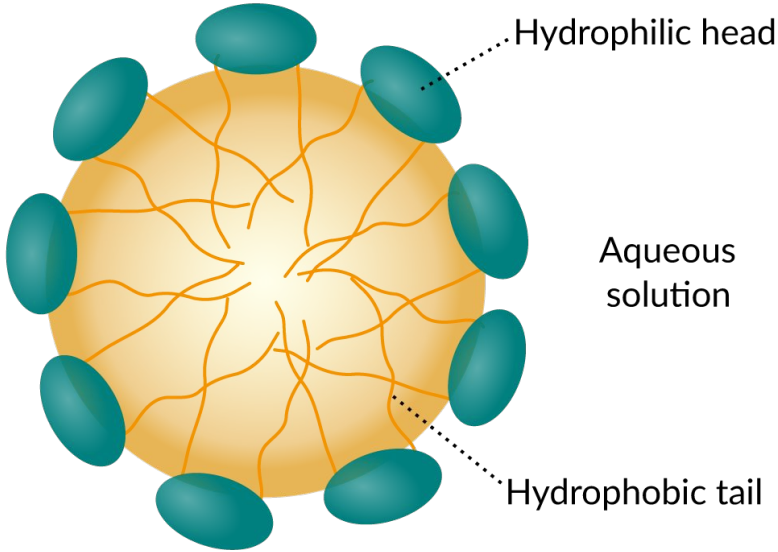
Can’t change how washing machines work.
(Washing cycles, time, agitation, etc.)

Costs must not be too high.

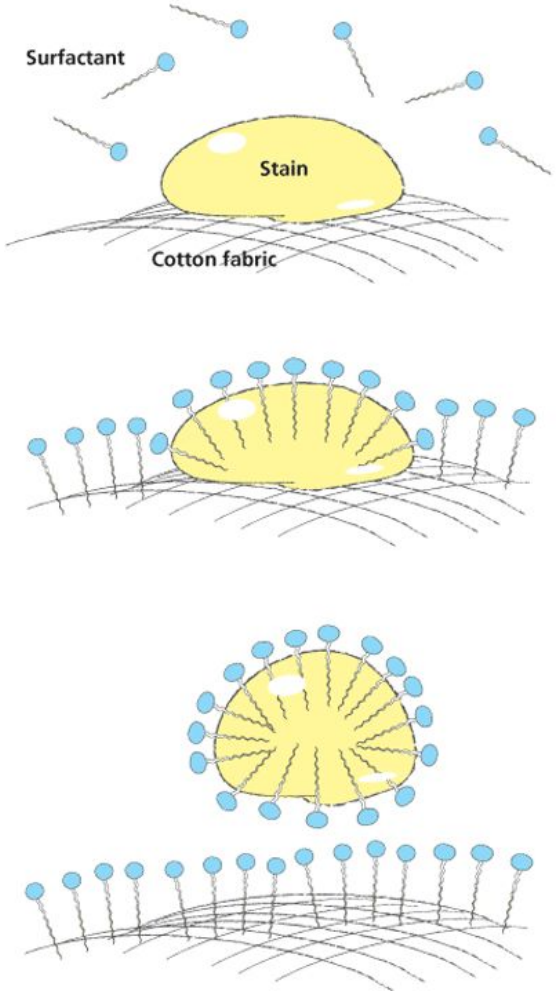
Avoid problematic ingredients.
(Phosphates, EDTA, VOCs, certain glycol ethers, alkylphenol ethoxylates, …)

How does laundry detergent work?

Surfactants reduce interfacial tension and form micelles.



Modified from (CC-BY-SA) Emmanuel Boutet.
https://en.wikipedia.org/wiki/File:Micelle_scheme-en.svg



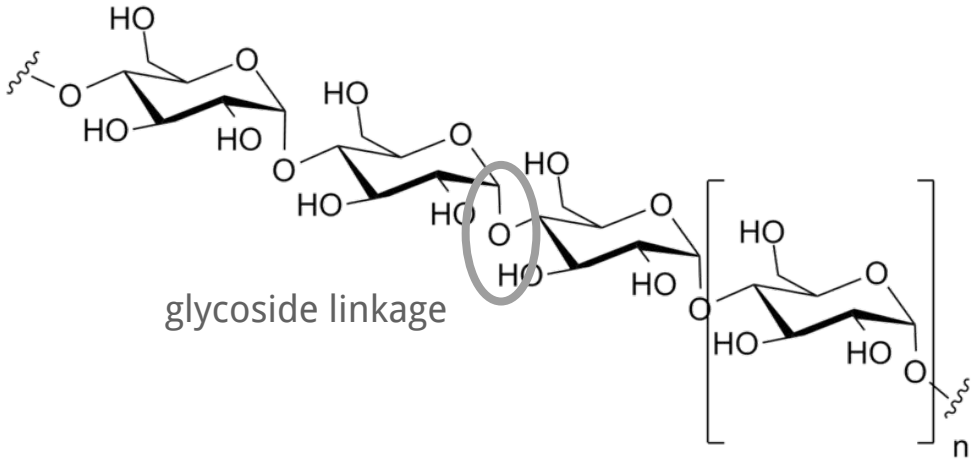
courtesy of Procter & Gamble

Solvents help break up soils and make them more soluble.

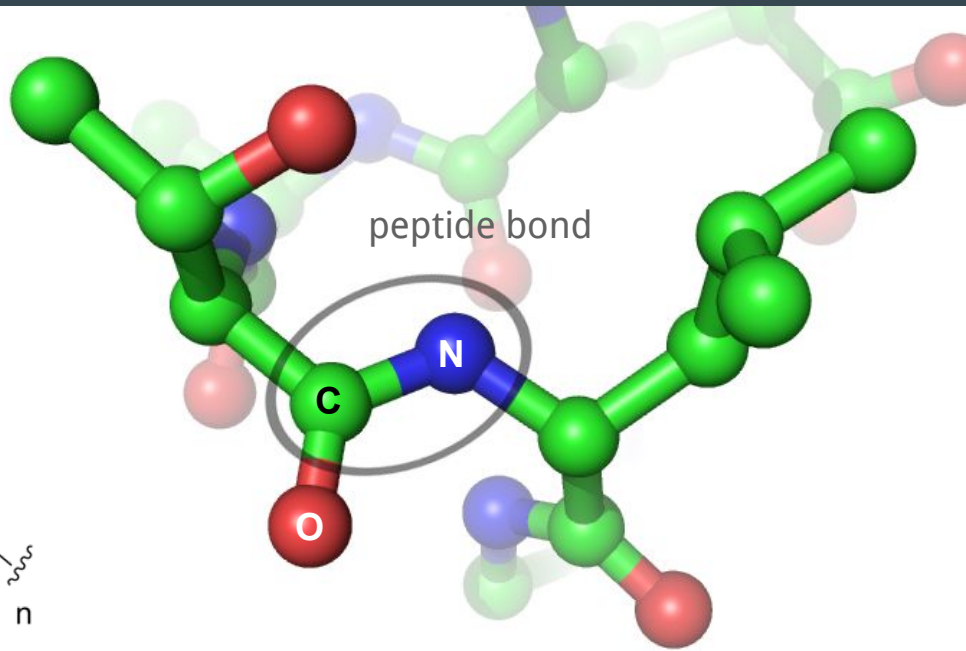
Dispersants keep the oily soil suspended and prevent re-deposition.

Enzymes chemically degrade soils, making them easier to remove.

Sugars



Proteins



Amylose (image by glycoform). https://en.wikipedia.org/wiki/File:Amylose_3Dprojection.corrected.png

(CC-BY-SA) webridge. https://en.wikipedia.org/wiki/File:Peptide_bond.png

Method Laundry 4x - ingredients of interest

Surfactants	Major health concerns
soy methyl ester ethoxylate (MEE)	Unknown: proprietary material; severe data gaps.
lauryl ethoxylate (LAE) *and* **PEG 600 monooctyl ether**	Skin & eye irritant; damage to mucous membranes. Aquatic toxicity (low/moderate).
sodium lauryl sulfate (SLS)	Acutely toxic & irritant to eyes & skin. Aquatic and terrestrial ecotoxicity (moderate/high).
Solvents	
limonene [also a fragrance]	Indoor air quality: volatile, oxidizes, respiratory & dermal irritant & sensitizer. Aquatic toxicity.
glycerol *and* **1,2-propanediol**	Acutely toxic when ingested at high doses (low risk).
monoisopropanolamine (1-amino-2-hydroxypropane)	Skin and eye damage (but low risk due to low concentration).

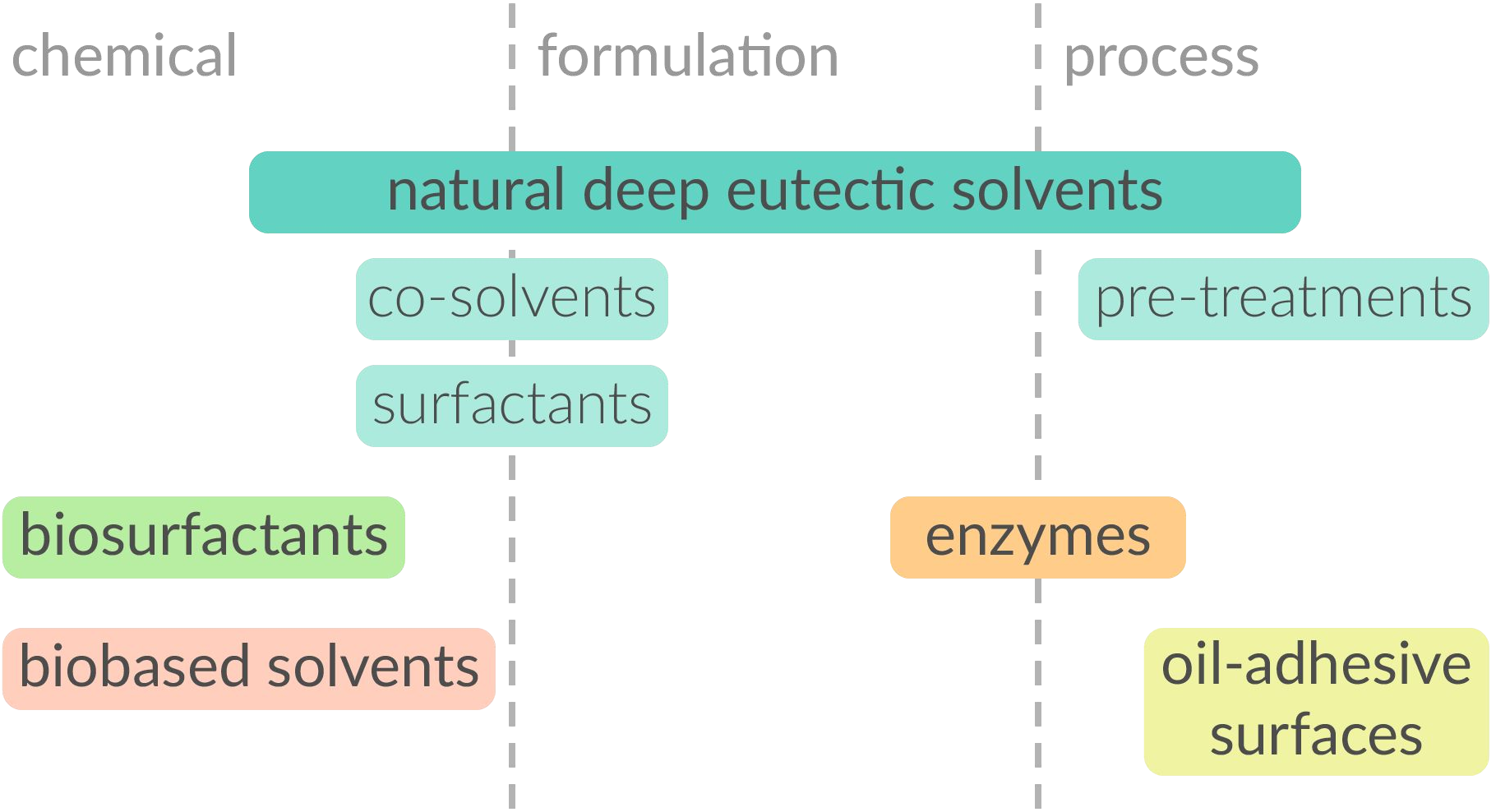
We approach the challenge on three levels

Challenge
Background
Strategies
Conclusion

chemical

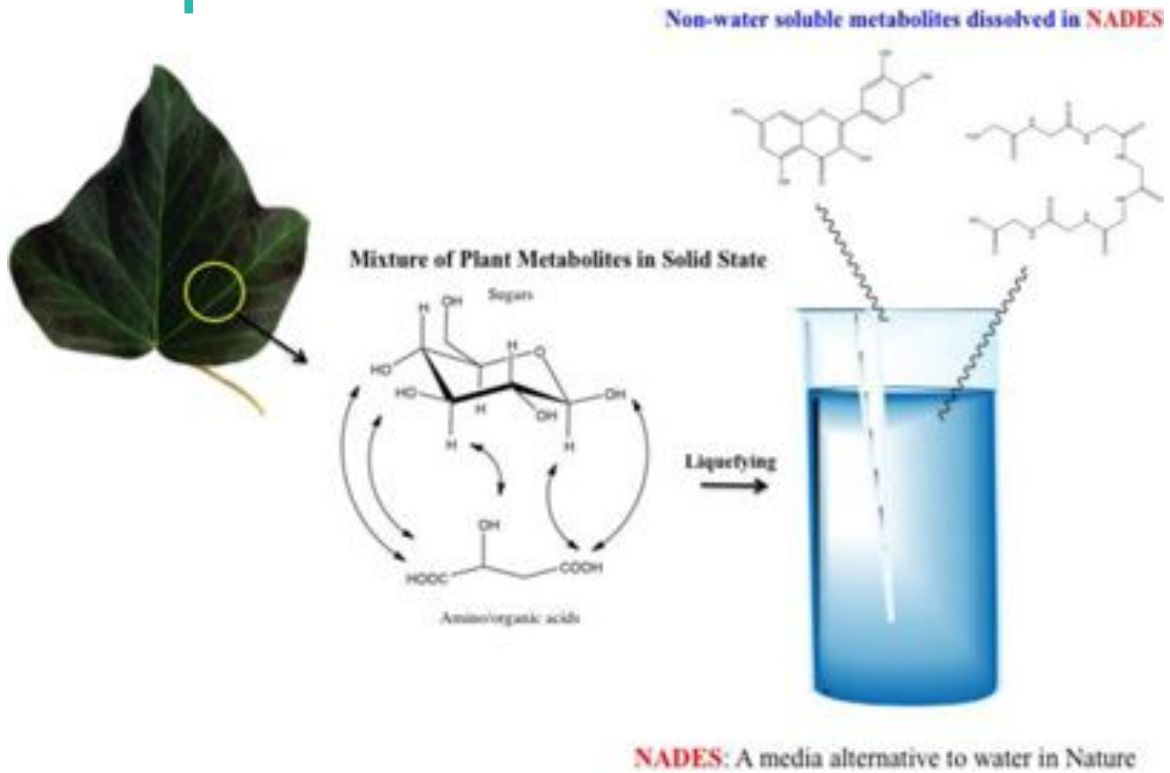
formulation

process


chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

Natural deep eutectic solvents (NADES)

NADES are bioinspired

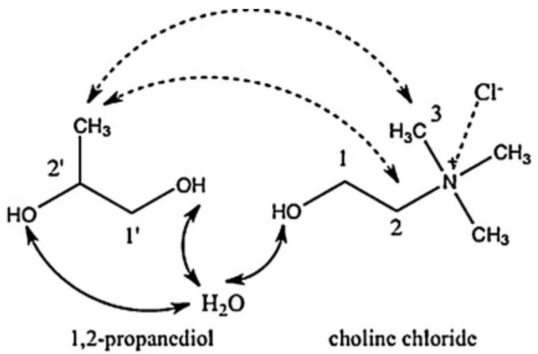


Dai, Y., van Spronsen, J., Witkamp, G.-J., Verpoorte, R., & Choi, Y. H. (2013). Natural deep eutectic solvents as new potential media for green technology. *Analytica Chimica Acta*, *766*, 61–68. http://doi.org/10.1016/j.aca.2012.12.019

“Eutectic” means depressed melting point

Hydrogen bonds form between acceptors and donors in the mixture.

The mixture has a **melting point lower** than each component.



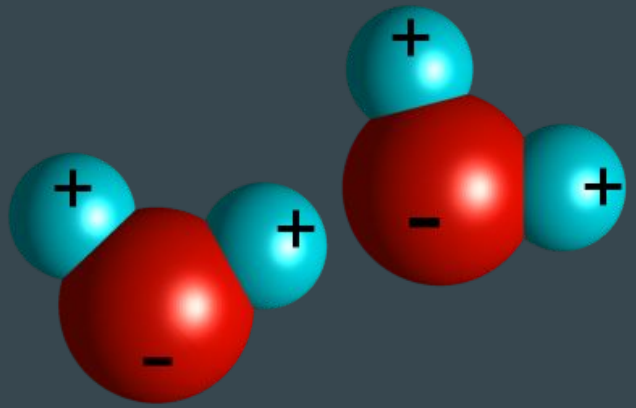
Chemical 1	Chemical 2	Molar ratio	Melting pt. (°C)
glycerol	choline chloride	3:1	**20**
glycerol	choline chloride	2:1	**23**
urea	choline chloride	2:1	**12**

Dai, Y., van Spronsen, J., Witkamp, G.-J., Verpoorte, R., & Choi, Y. H. (2013). Natural deep eutectic solvents as new potential media for green technology. *Analytica Chimica Acta*, *766*, 61–68. http://doi.org/10.1016/j.aca.2012.12.019

Natural deep eutectic solvents (NADES)

NADES interact with water

- Hydrogen bonding property allows for incorporation of water molecules into NADES structure

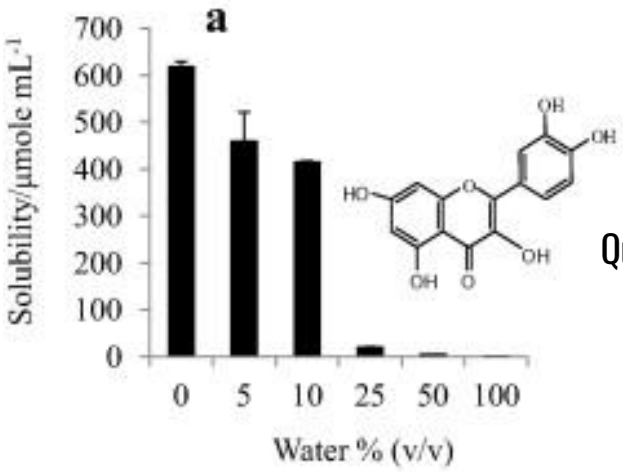


- Affects properties
  - Viscosity
  - Conductivity
  - Polarity

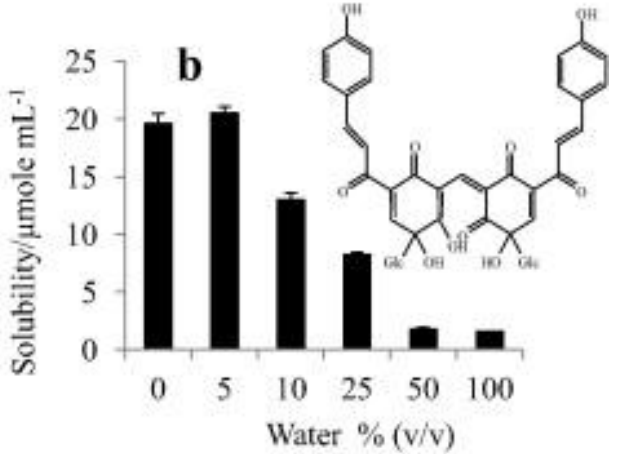
Do NADES maintain their structure in high quantities of water?

Natural deep eutectic solvents (NADES)

NADES can solubilize hydrophobic materials



Quercetin



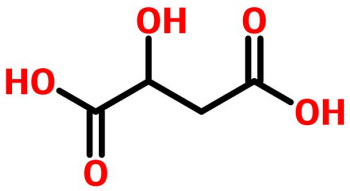
Carthamin

Dai, Y., Witkamp, G.-J., Verpoorte, R., & Choi, Y. H. (2015). Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. Food Chemistry, 187, 14–19. http://doi.org/10.1016/j.foodchem.2015.03.123

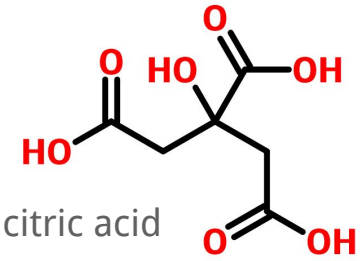
NADES strategy #1

Use NADES as co-solvents

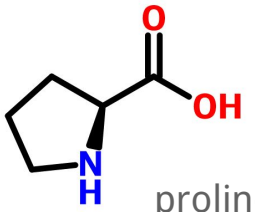
Already known to form NADES:



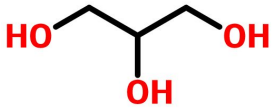
malic acid



citric acid

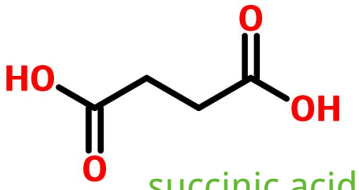


proline

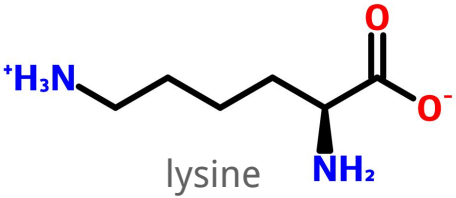


glycerol

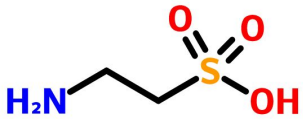
Potential (untested) NADES components:



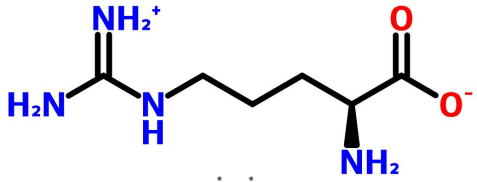
succinic acid



lysine



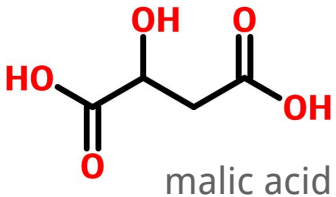
taurine



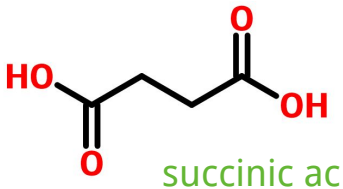
arginine

NADES strategy #2

Use NADES as dispersants or surfactants

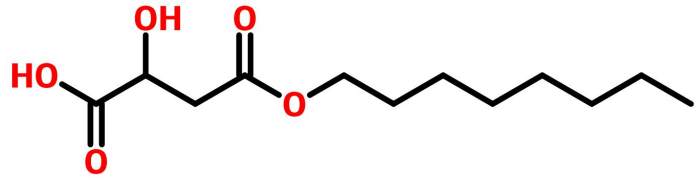


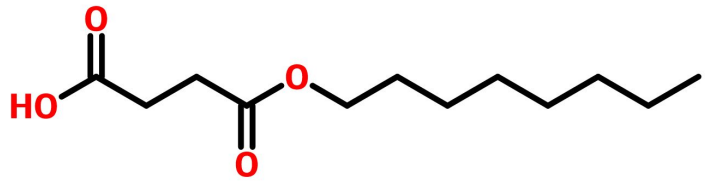
malic acid



succinic acid
(biobased)

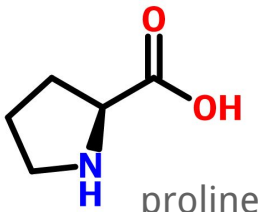
esterification with
C_8-C_{10} alcohols



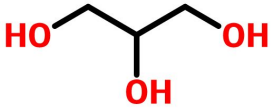


potential amphiphilic NADES components

Combine with:



proline



glycerol

etc.

NADES strategy #3

Pre-treatment using NADES

A pre-treatment formulation based on NADES will be **highly concentrated,** potentially lifting out oily soils in advance of cold washing.

Natural deep eutectic solvents (NADES)

Toxicity

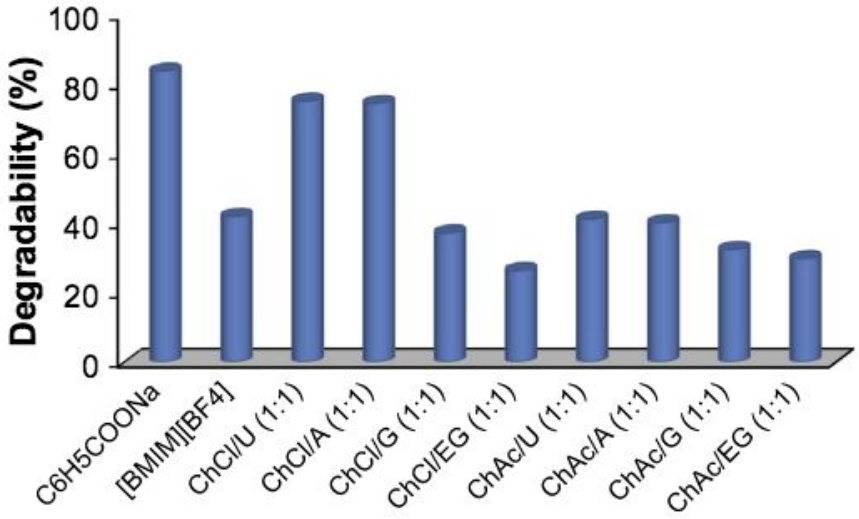
- Low to moderate cytotoxicity
- Low phytotoxicity

- Toxicity may be dependent upon chemical make up

- Toxicity of NADES lower than toxicity of individual parts

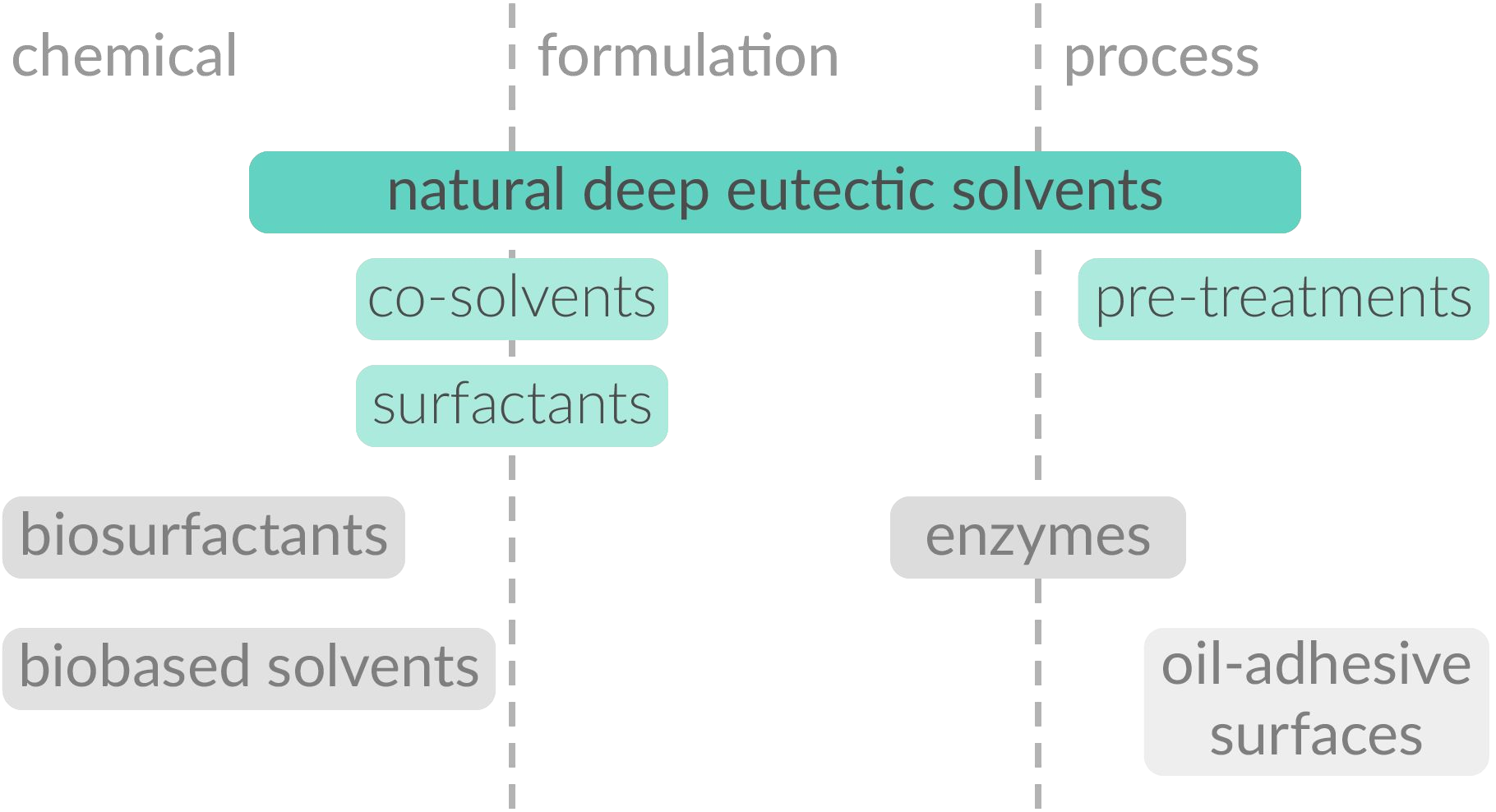
Biodegradability

- ChCl:Gly > ChCl:Glc > ChCl:OA



Wen, Qing, Jing-Xin Chen, Yu-Lin Tang, Juan Wang, and Zhen Yang. “Assessing the Toxicity and Biodegradability of Deep Eutectic Solvents.” *Chemosphere* 132 (August 2015): 63–69.

Radošević, Kristina, Marina Cvjetko Bubalo, Višnje Gaurina Srček, Dijana Grgas, Tibela Landeka Dragičević, and Ivana Radojčić Redovniković. “Evaluation of Toxicity and Biodegradability of Choline Chloride Based Deep Eutectic Solvents.” *Ecotoxicology and Environmental Safety* 112 (February 2015): 46–53.

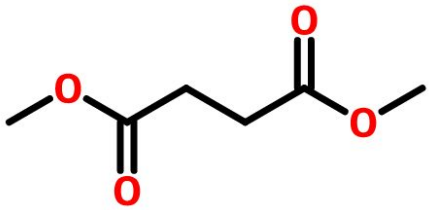

chemical
formulation
process
natural deep eutectic solvents
co-solvents
surfactants
pre-treatments
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

Bio-based solvents

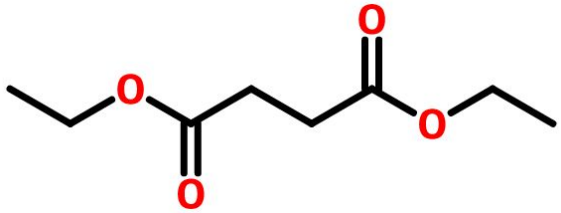
Biobased solvents

Dialkyl succinic acid esters from renewable feedstocks

Short

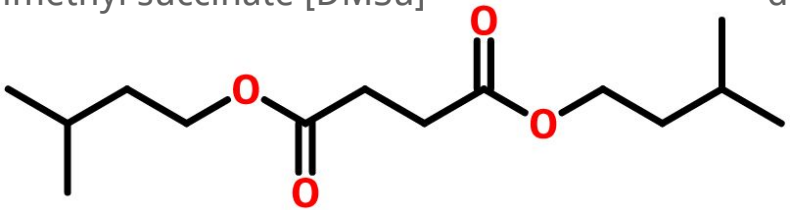


dimethyl succinate [DMSu]



diethyl succinate [DESu]

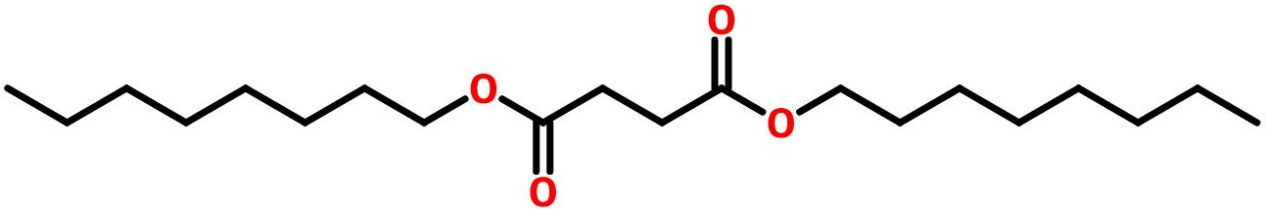
Medium



bis(3-methylbutyl) succinate [D(3MB)Su]

bioamber™

Long

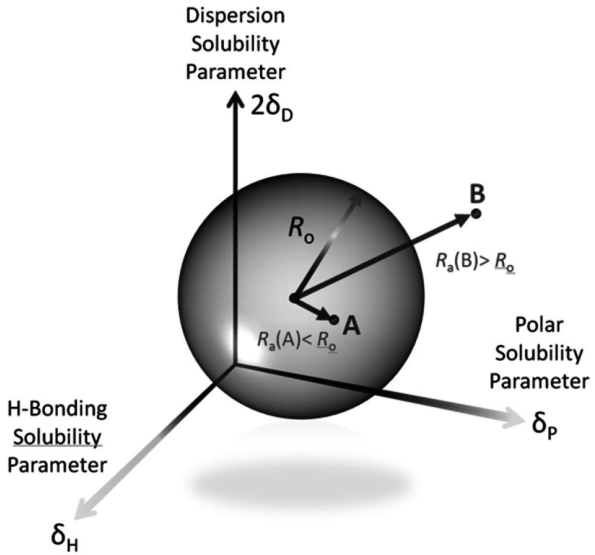


dioctyl succinate [DOSu]

Solvent properties can be matched with soils

substance	δ[D]	δ[P]	δ[H]
dimethyl succinate°	16.2	4.7	8.4
carbonized residue°	*18.7*	*7.5*	*8.9*
diethyl succinate‡	13–16	4–10	8
cottonseed oil°	*12.2*	*5.8*	*5.8*
bis(3-methylbutyl) succinate‡	13-15	3–9	6–7
olive oil°	*15.9*	*1.2*	*5.4*
dioctyl succinate‡	16	2–7	3–5
saturated fat (lard)°	*17.7*	*2.7*	*4.7*

Hansen Solubility Parameters
(HSP) [MPa½]



‡ = Estimated. ° = Hansen, C. M. (2007). *Hansen solubility parameters: a user's handbook* (2nd ed). Boca Raton: CRC Press.

Biobased solvents

Human & ecological toxicity

Significant **data gaps**, but **low concern** overall.

- DMSu is used as a food additive.
- Inhalation of DMSu can cause acute respiratory toxicity.

Low exposure potential:

- These solvents are **semivolatile.**

Flammability: **low**, **moderate** [DMSu].

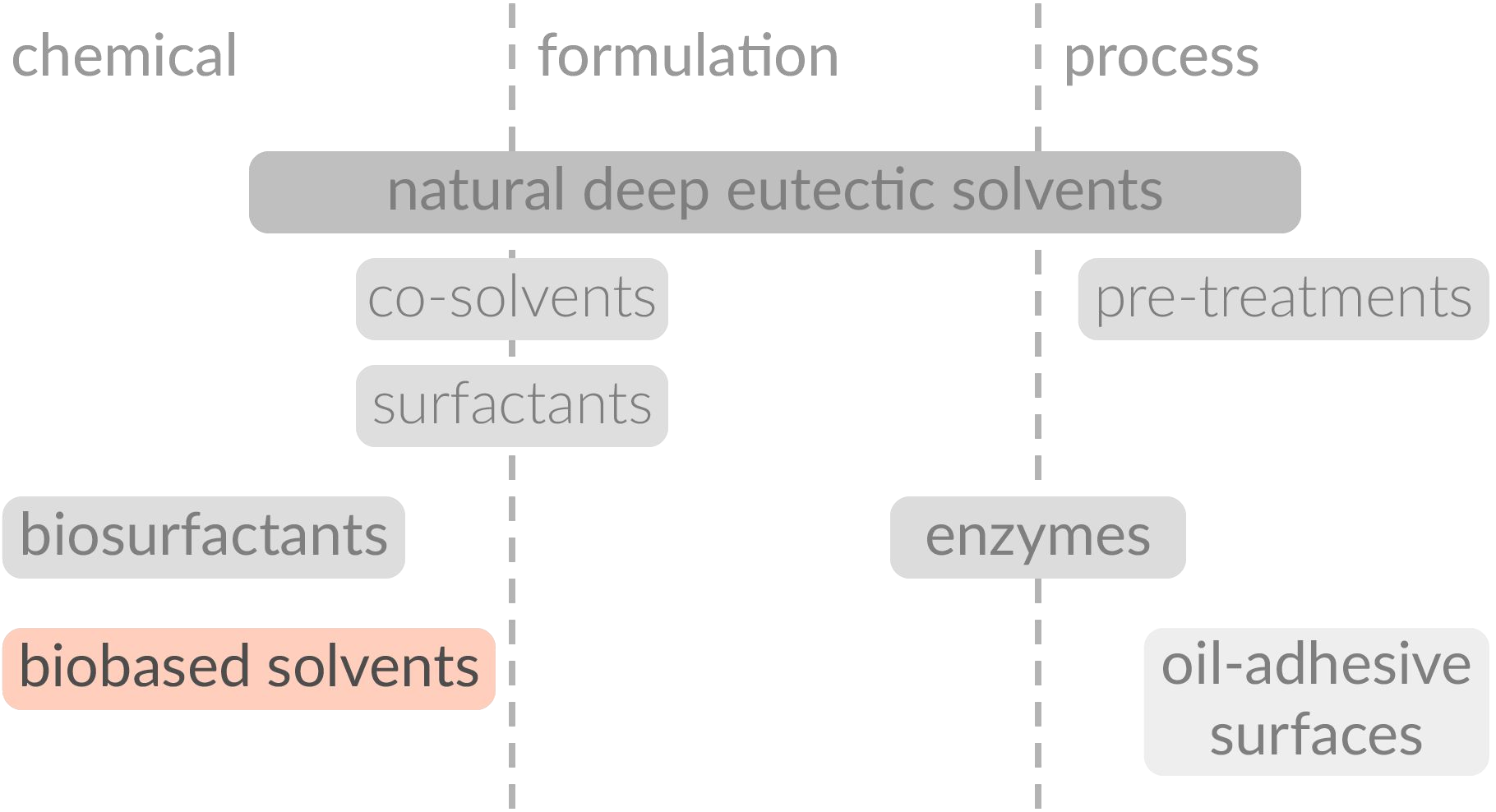
Environmental fate

Persistence:

- **Ready biodegradability** expected.
- Persistence **could be high** in the absence of biodegradation.
- Overall persistence: 17-28 days

Bioaccumulation:

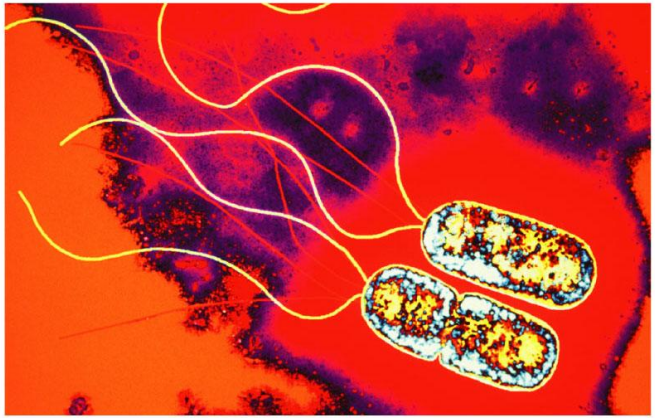
- **Very low** [DMSu, DESu]
- **Low** [D(3MB)Su]
- **moderate or low** [DOSu]

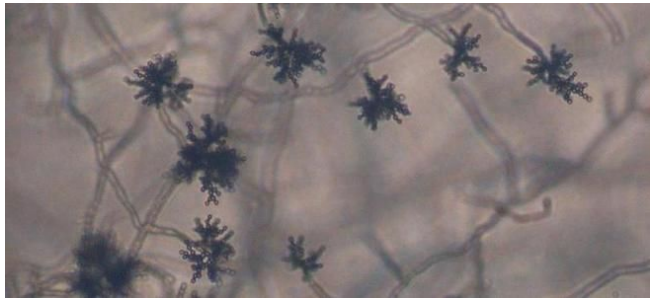

chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

Biosurfactants

Biosurfactants

Bacteria and fungi use multi-purpose surfactants





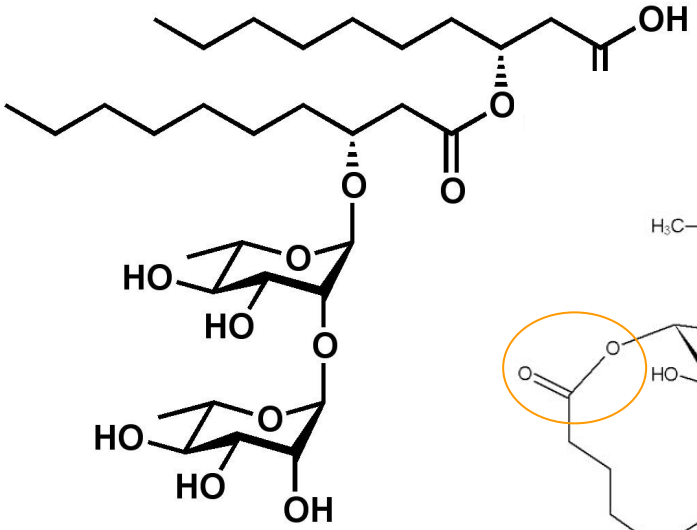
Cladosporium sp. on agar. (CC-BY-SA) Keisotyo. http://en.wikipedia.org/wiki/File:Cladosporium_sp_conidia.jpg

Nutrient intake. Solubilize hydrocarbons in aqueous environments for digestion

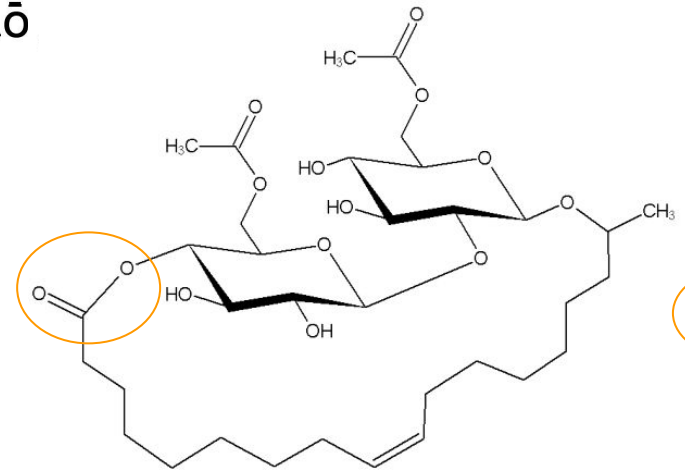
Substrate interaction. Attach to hydrophobic substrates to facilitate growth

Community organization. Organize porous structured biofilms

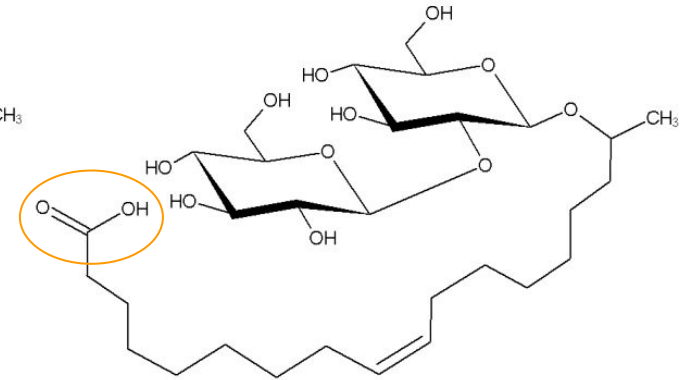
Glycolipids are one class of surfactants found in nature



Rhamnolipid 1



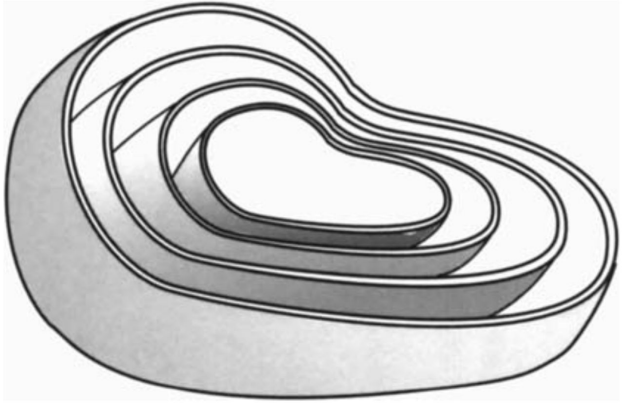
Lactonic sophorolipid



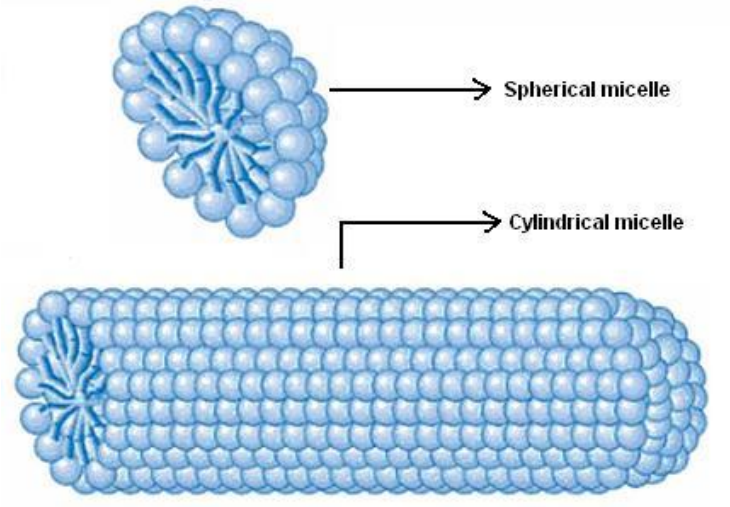
Acidic sophorolipid

Biosurfactants form 3D structures in solution

Useful for detergent formulations?



Lamellar vesicles



Penfold, J., et al. (2011). Solution Self-Assembly of the Sophorolipid Biosurfactant and Its Mixture with Anionic Surfactant Sodium Dodecyl Benzene Sulfonate. *Langmuir, 27*(14), 8867–8877. http://doi.org/10.1021/la201661y

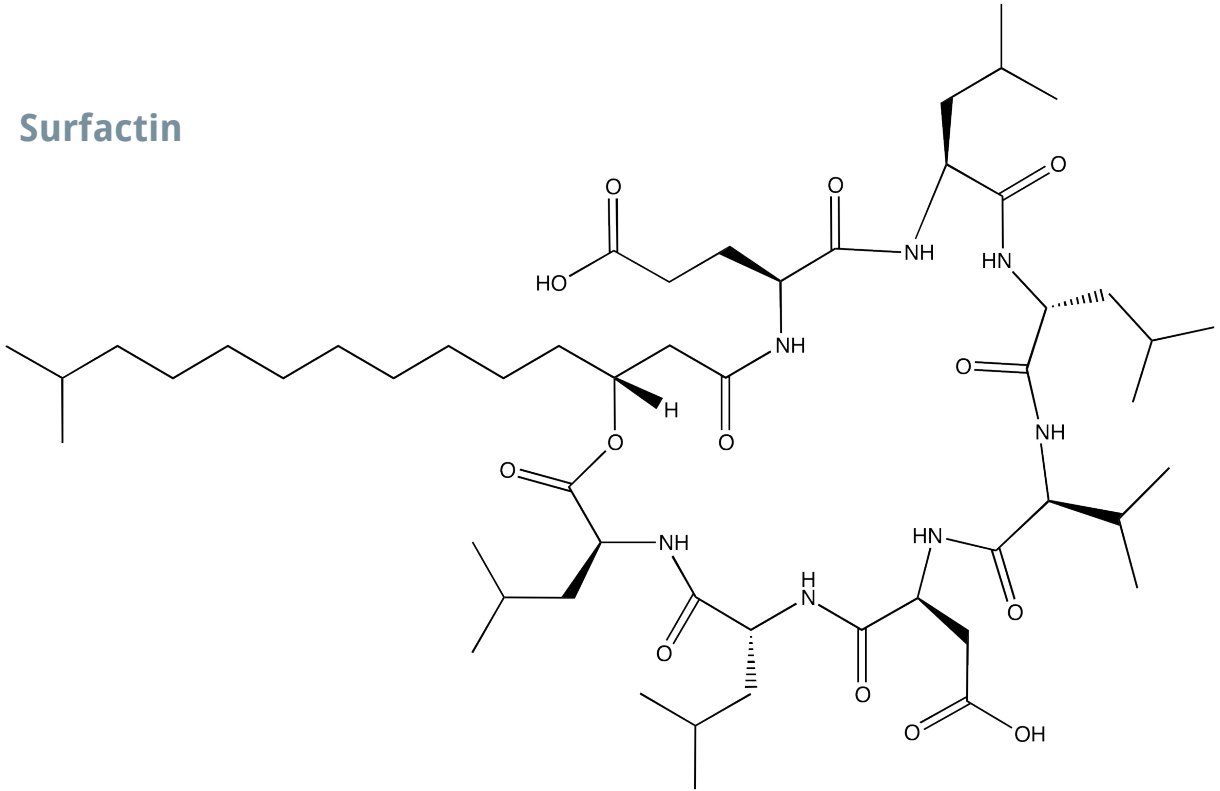
Lamellar vesicle image: Ho, L. T. T. (2000). *Formulating detergents and personal care products: a [complete] guide to product development.* Champaign, Ill.: AOCS Press.

http://image.tutorvista.com/cms/images/44/Micelle.JPG

Biosurfactants

Another kind of surfactant found in nature: lipopetide

Surfactin



https://upload.wikimedia.org/wikipedia/commons/a/a7/Surfactin.png

Biosurfactants

Additivity with other detergent components at low temperatures

Promising avenue for a formulation approach?

Mukherjee (2007). Potential application of cyclic lipopeptide biosurfactants produced by Bacillus subtilis strains in laundry detergent formulations. *Letters in Applied Microbiology 45*, 330-335. doi:10.1111/j.1472-765X.2007.02197.x

Biosurfactants

Promising surfactants from renewable sources

Equal or higher performance, more biodegradable, less toxic than synthetic surfactants

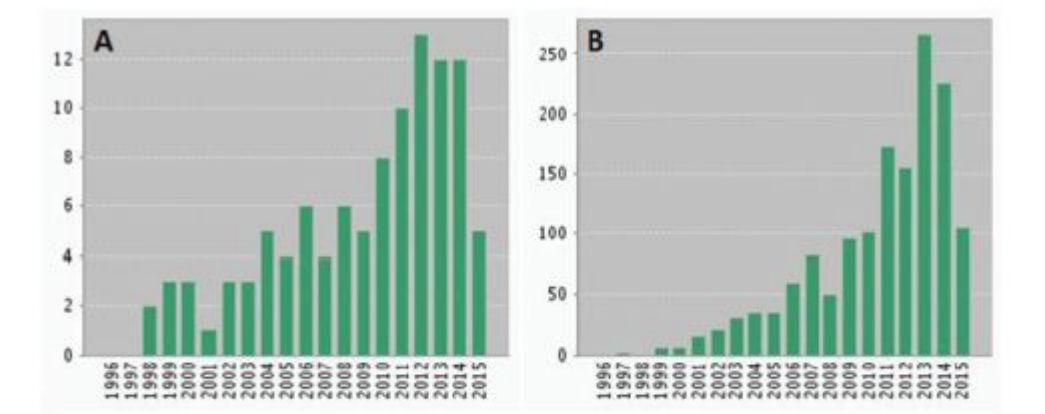


Fig. 1 Number of publications (A) and citations (B) per year on sophorolipids.

Delbeke, et al. (2015). Chemical and enzymatic modification of sophorolipids. *Green Chem.* http://doi.org/10.1039/C5GC02187A

Challenge: large-scale production costs

Biosurfactants

Many recent efforts to optimize production

Jeanne Pemberton, University of Arizona

NatSurFact, Logos Technologies

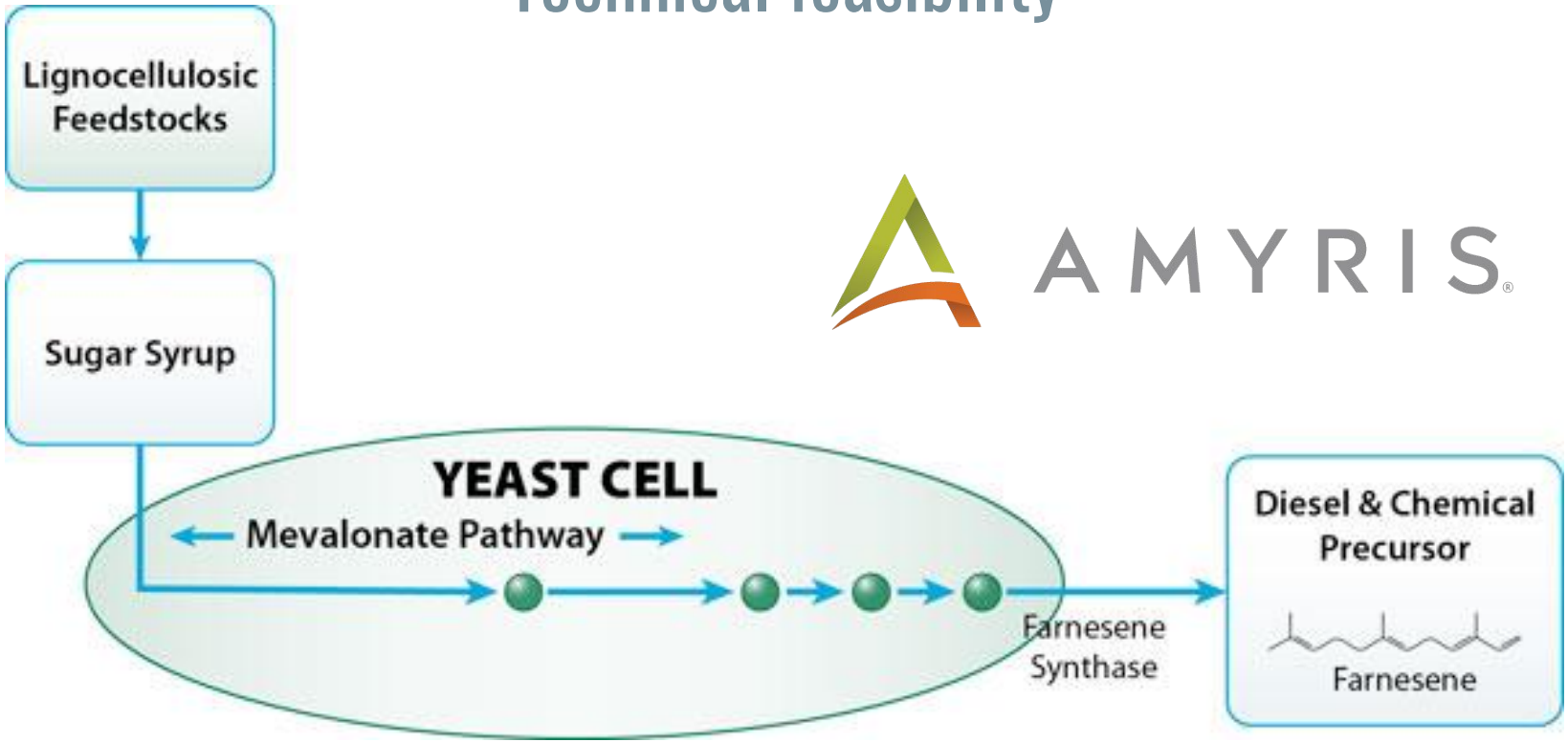
http://greenchemicalsblog.com/2015/05/07/bio-based-surfactants-roundup/

ECOVER®

SARAYA

GLYCOSURF
INSPIRED BY NATURE

Technical feasibility



AMYRIS®

http://www.nabcprojects.org/images/amyris_graphic.jpg

Biosurfactants

Direct ingredient substitution

rhamnolipid or **sophorolipid**

Sodium lauryl sulfate (SLS), Lauryl ethoxylate, PEG 600 monooctyl ether, Soy methyl ester ethoxylate.

Biosurfactants

Low toxicity alternatives

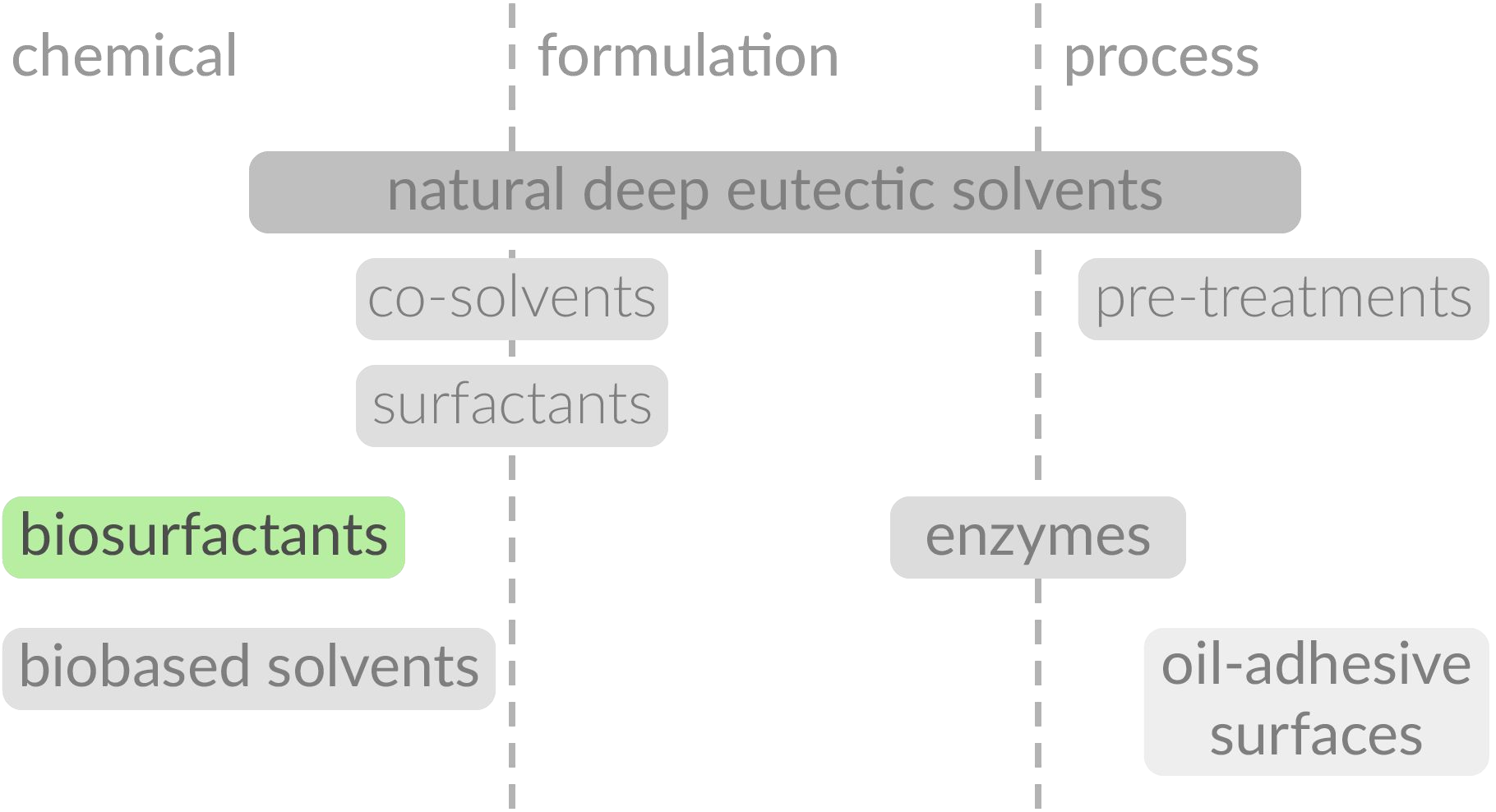
- Readily biodegradable
- Low cytotoxicity (human cells)
- Lower skin and eye irritation compared to conventional surfactants

Possible mild aquatic toxicity

- Lower than conventional surfactants

Delbeke, et al. (2015). Chemical and enzymatic modification of sophorolipids. *Green Chem.* http://doi.org/10.1039/C5GC02187A

Hirata ,et al. (2009). Novel characteristics of sophorolipids, yeast glycolipid biosurfactants, as biodegradable low-foaming surfactants. *Journal of Bioscience and Bioengineering* 108(2), 142-146. doi:10.1016/j.jbiosc.2009.03.012


chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

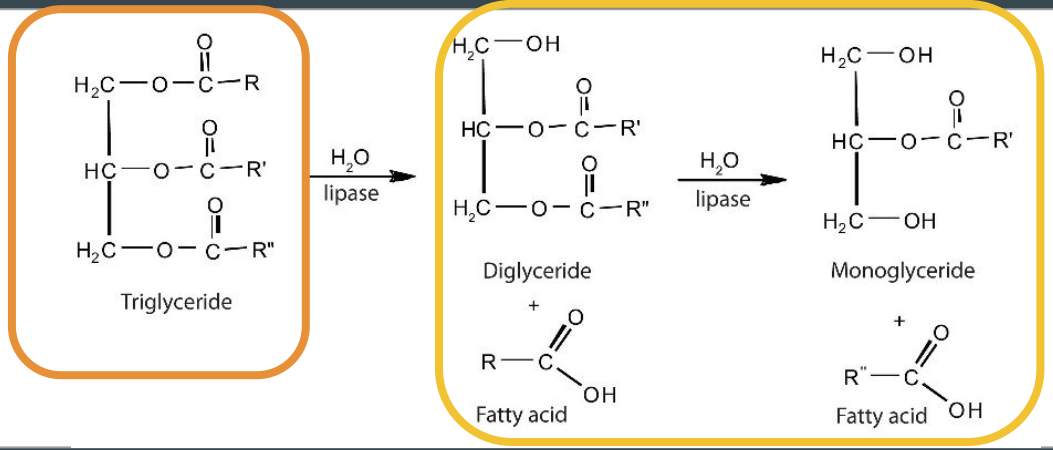
Enzymes


NADES
Biobased solvents
Biosurfactants
Enzymes
Oil-adhesive surfaces

In nature, enzymes degrade proteins, sugars and lipids by breaking bonds.

Enzymes

In laundry applications, enzymes interact in combination to break apart complex, hydrophobic compounds



- Lipase functions by hydrolyzing triglycerides into glycol and free fatty acids
- Lipase may break down fats more effectively than current ingredients at low temperatures

Technical constraints

- A slower reaction time[1]
- A malodor: butyric acid[1]
- Duration of activity: continues into the drying cycle[1]
    - Optimum activity of lipase at 20-30% water content

Stabilizing ingredients such as diols and calcium chloride also needed

1. Aehle, Wolfgang. (2004) *Enzymes in Industry: Production and Application.* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. 172-174

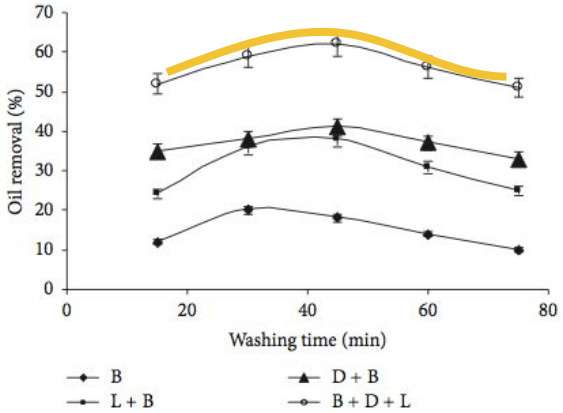
Enzymes

New lipase strains present opportunities

- Lipex produced by Novozymes engineered to be most effective in the first wash[1]
  - Effective at 20 C

- *Staphylococcus arlettae* JPBW- 1 provides optimal oil removal in combination with nonionic surfactants as well as oxidizing agents[2]
  - Optimum temperature range is 25-100 C, with maximum oil removal activity at 37 C

http://www.hansengroup.biz/novozymes/index.php?cp=pl&lang=en



1. http://novozymes.com/en/news/news-archive/Pages/41098.aspx

2. Chauhan, M., Chauhan, R. S., & Garlapati, V. K. (2013). Evaluation of a New Lipase from Staphylococcus sp. for Detergent Additive Capability. *BioMed Research International, 2013.*

Enzymes

Process and formulation changes also present opportunities

Process Changes

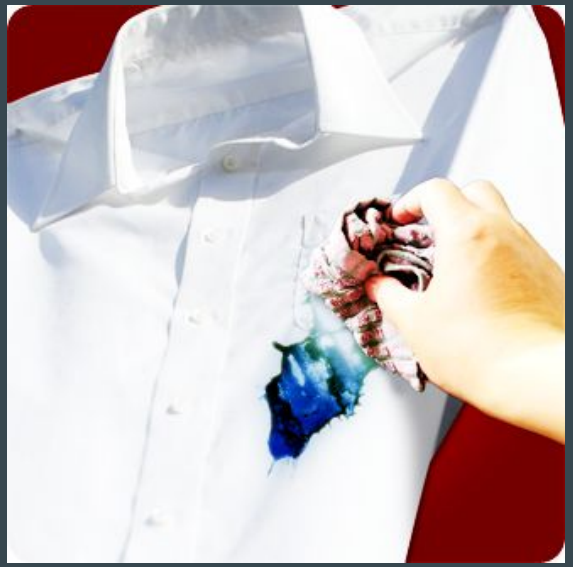
- Pre-Treatment

Synergism

- 1-30% by weight alkyl ester fatty acid sulfonate surfactants and nonionic surfactants[2]
- Protease and lipase interaction[1]

Antagonism

- Surface-active molecules such as surfactants and fatty acids/soaps can strongly inhibit lipase[2]



http://www.muctim.com.vn

1. Jiang H, Yin F, REn Y. (2002). Study on synergism of protease, lipase and cellulase used in detergents. *China Surfactant Detergent & Cosmetics*, 34(3):151-153, 2. Aehle, Wolfgang. (2004) *Enzymes in Industry: Production and Application.* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. 172-174

Enzymes

Low risk of human & environmental toxicity

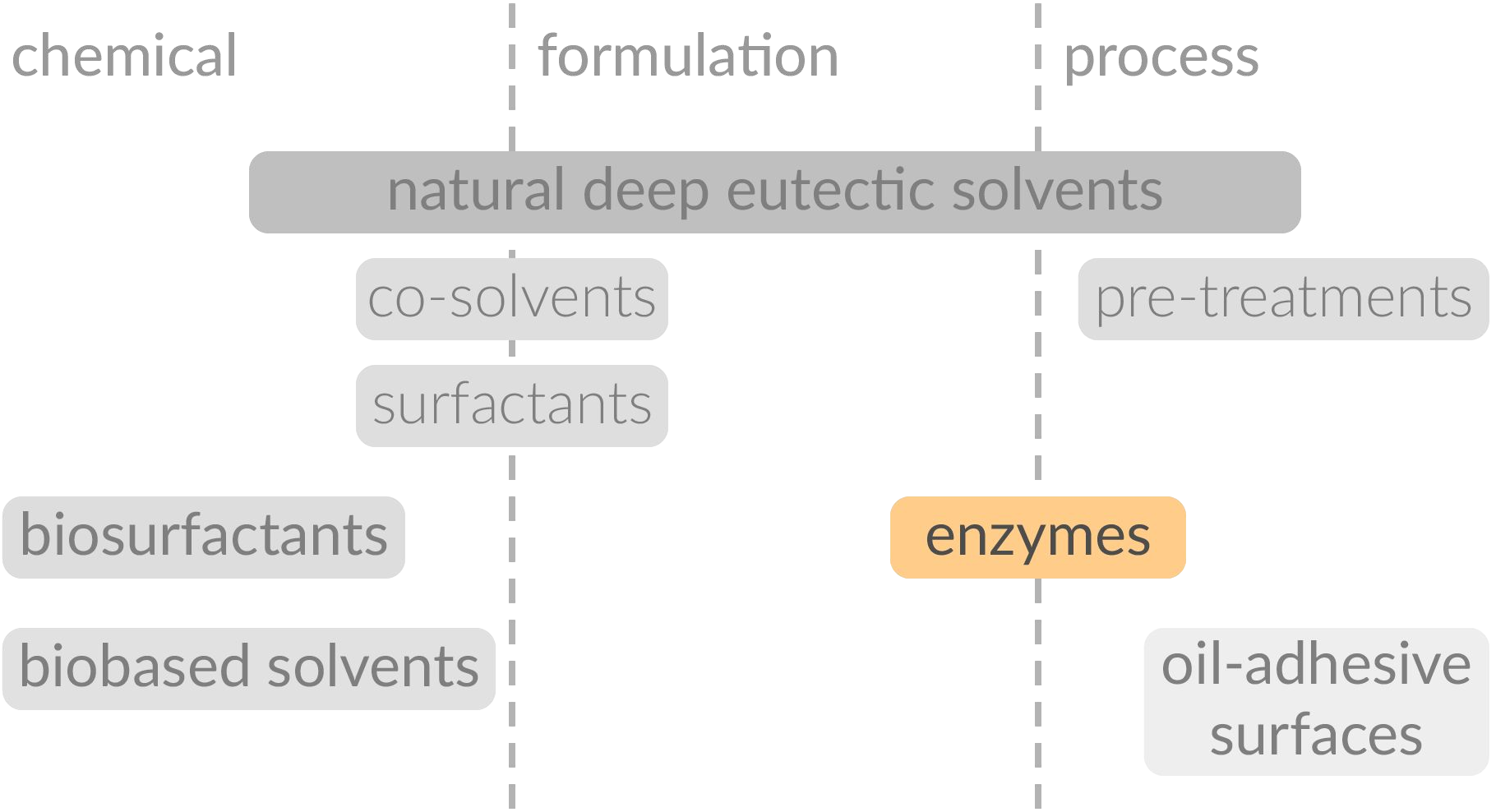
- Consumer exposure risk is low
- No evidence of
  - developmental toxicity
  - reproductive toxicity
  - carcinogenicity
- Low environmental toxicity and persistence

Basketter, D., Berg, N., Broekhuizen, C., Fieldsend, M., Kirkwood, S., Kluin, C., ... & Rodriguez, C. (2012). Enzymes in cleaning products: an overview of toxicological properties and risk assessment/management. *Regulatory Toxicology and pharmacology*, *64*(1), 117-123.

Respiratory Irritant & Sensitizer

Dermal Irritant & Sensitizer

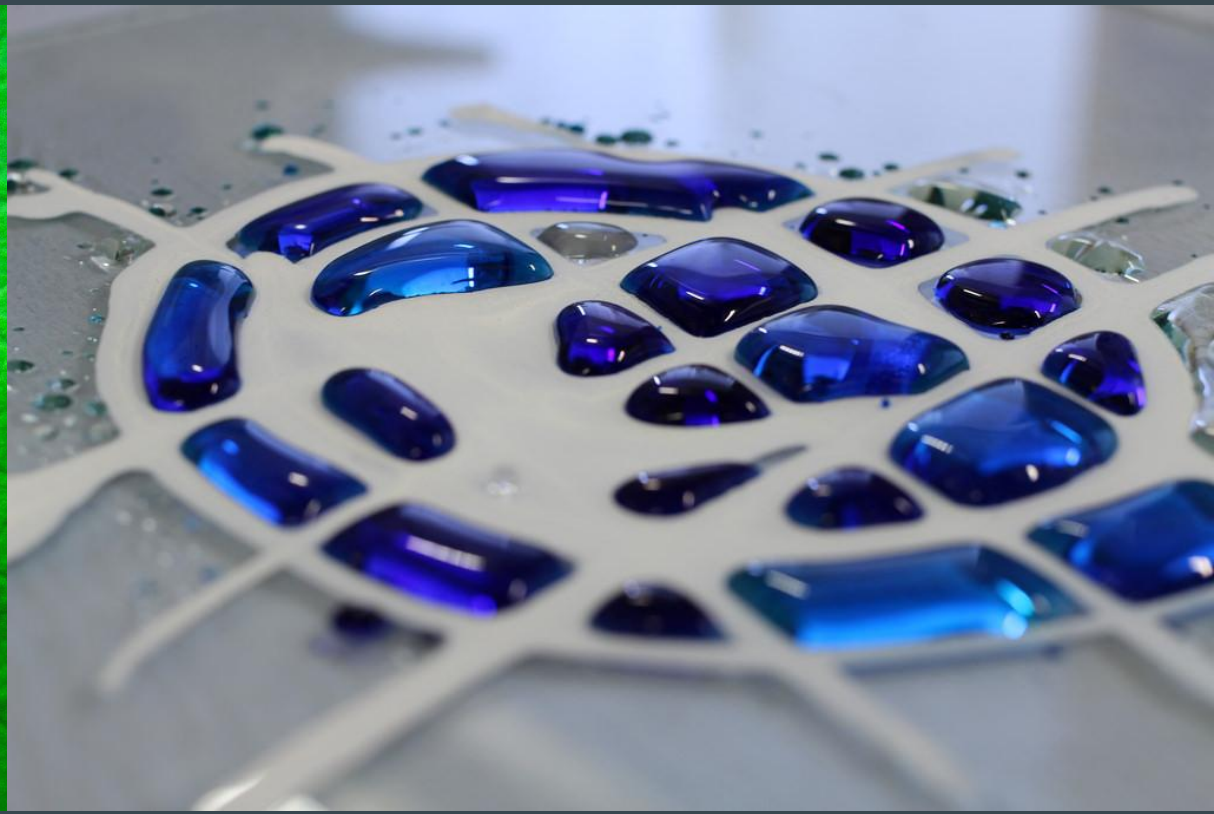
www.openclipart.org, www.puresafety.co.uk


chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

Oil-adhesive surfaces

Oil-adhesive surfaces

Superhydrophobic & superoleophobic surfaces

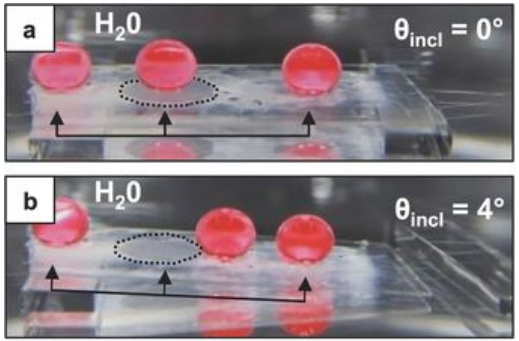


Oil-adhesive surfaces

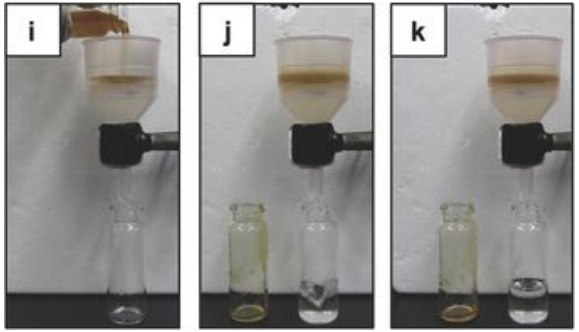
Functionalized multi-layered polymer coatings create **superhydrophobic** or **superoleophobic** surfaces.

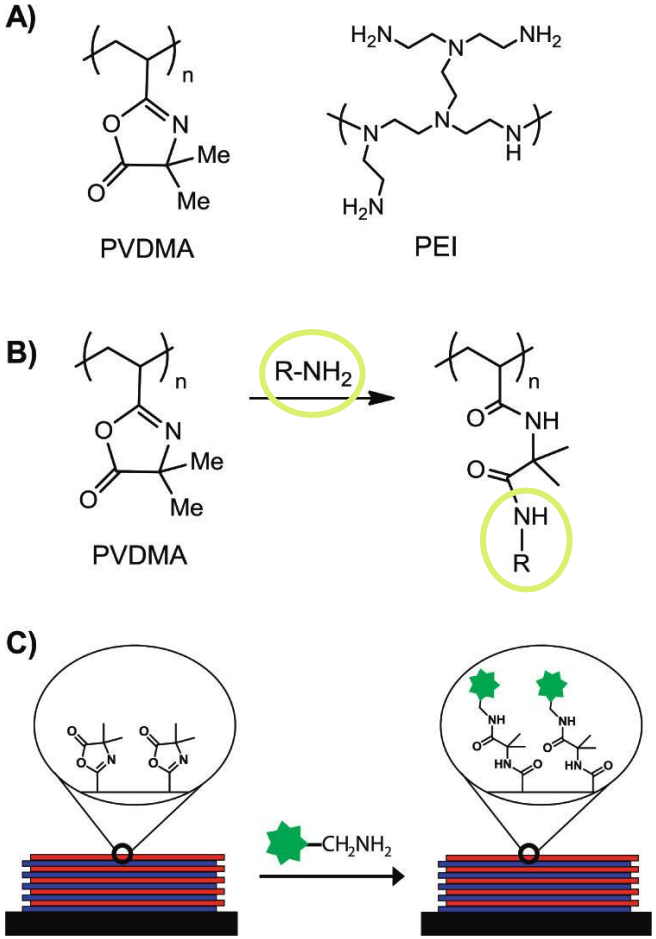
… with different degrees of **oil-adhesiveness, even while underwater.**

R-NH_2 = propylamine



R-NH_2 = glucamine



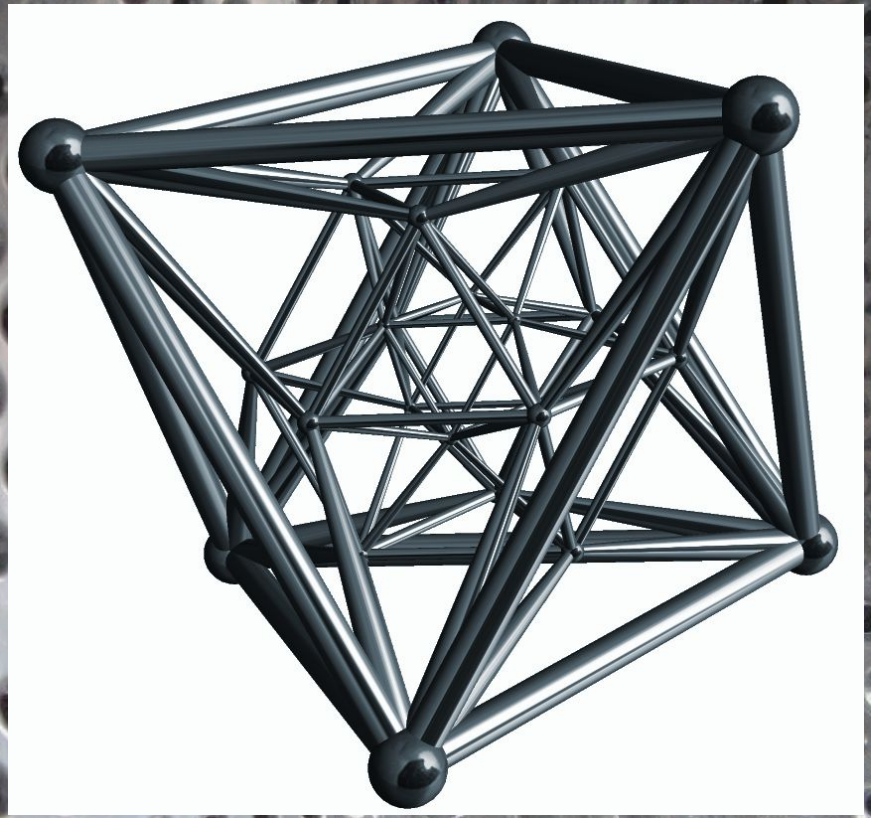


Broderick, A. H., Manna, U., & Lynn, D. M. (2012). Covalent Layer-by-Layer Assembly of Water-Permeable and Water-Impermeable Polymer Multilayers on Highly Water-Soluble and Water-Sensitive Substrates. *Chemistry of Materials, 24*(10), 1786–1795. http://doi.org/10.1021/cm300307g

Manna, U., & Lynn, D. M. (2015). Synthetic Surfaces with Robust and Tunable Underwater Superoleophobicity. *Advanced Functional Materials, 25*(11), 1672–1681. http://doi.org/10.1002/adfm.201403735

Oil-adhesive surfaces

Exploit reversible oil adhesion to capture & remove soil



Product concept

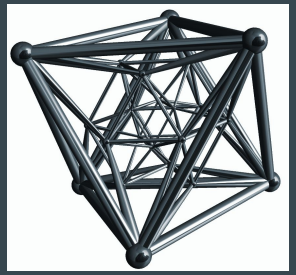
Durable, reusable object.

Liquid-permeable with **high surface area.**

Superoleophobic oil-adhesive coating on interior surfaces.

Regenerate with small quantities of a safe degreasing formulation.

Oil-adhesive surfaces



Areas of concern

Product life-cycle stewardship.

Life-cycle chemical impacts: polymer derived from **aziridine** (carcinogen, mutagen, acutely toxic).

How? Shifts the oily soil removal challenge to a secondary application, with higher consumer exposure potential to solvents.

Product concept

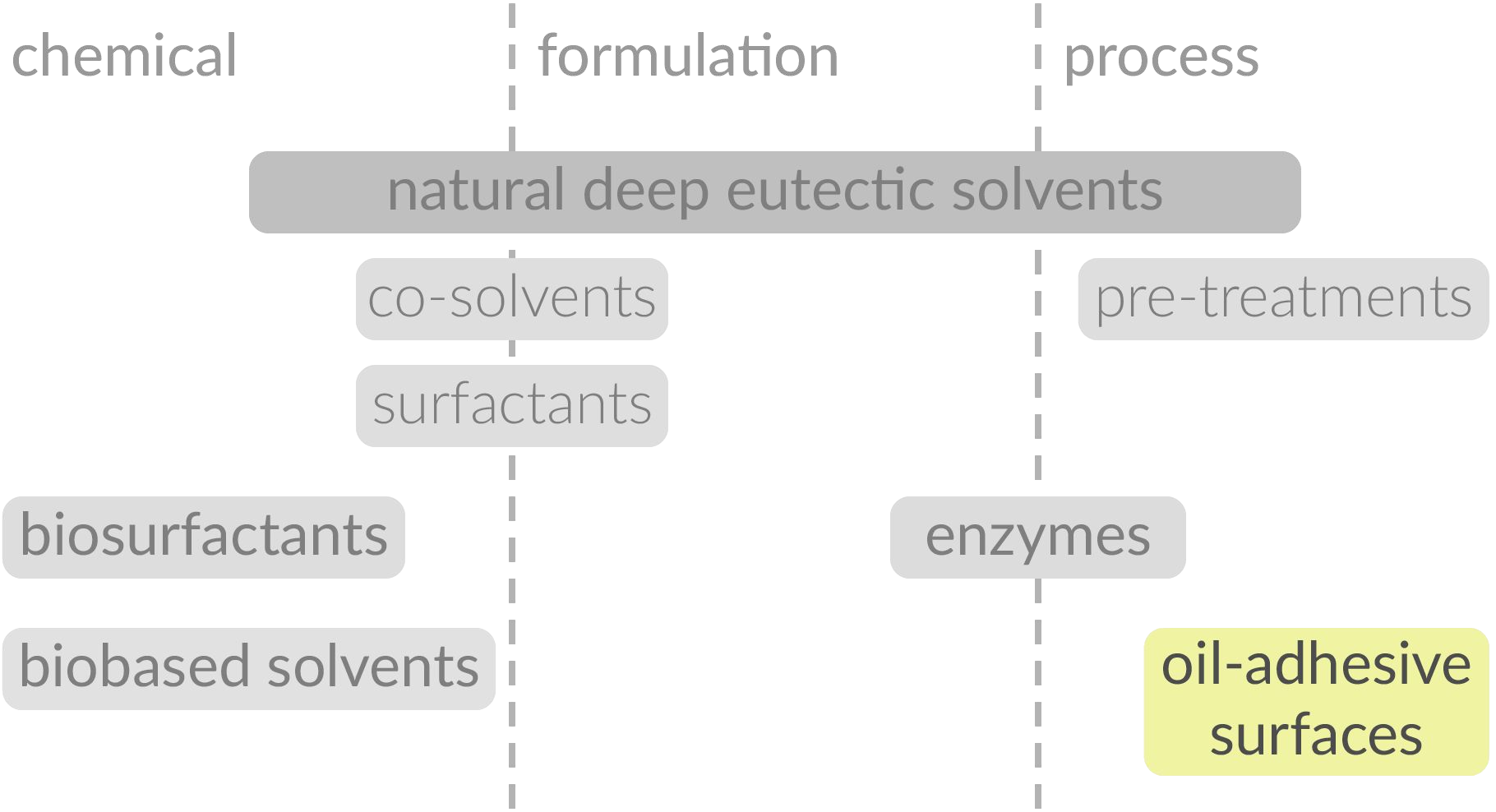
Durable, reusable object.

Liquid-permeable with **high surface area.**

Superoleophobic oil-adhesive coating on interior surfaces.

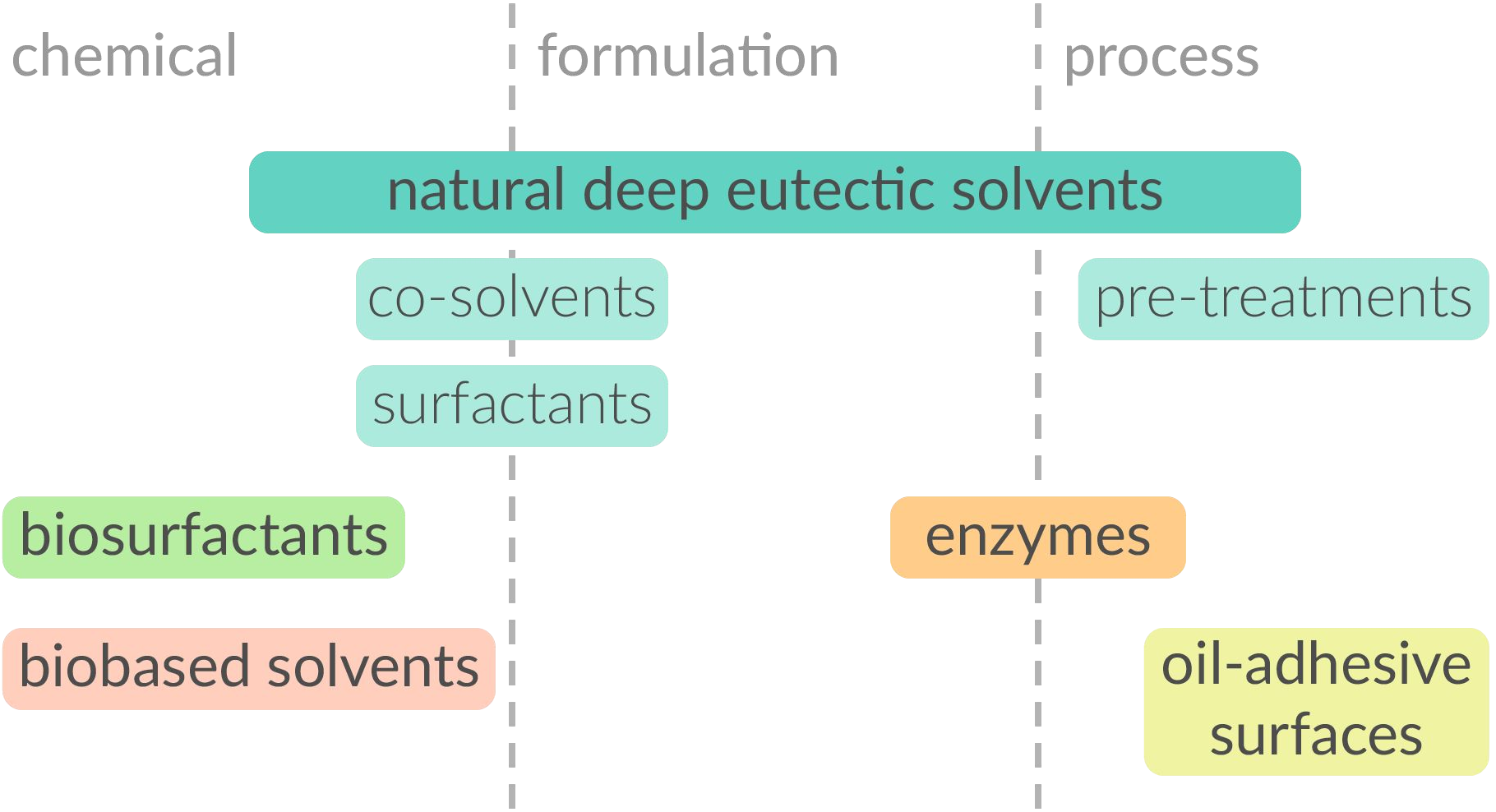
Regenerate with small quantities of a safe degreasing formulation.

- **Product as a service**
- **Cradle-to-cradle design**

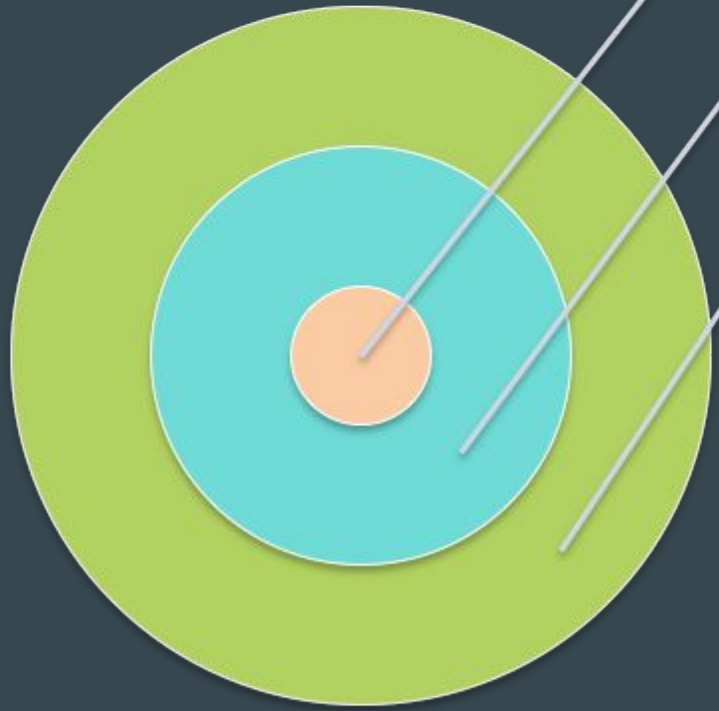

chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

We have identified 5 strategies that our partners may pursue depending on their preferences.

Challenge
Background
Strategies
Conclusion


chemical
formulation
process
natural deep eutectic solvents
co-solvents
pre-treatments
surfactants
biosurfactants
enzymes
biobased solvents
oil-adhesive surfaces

Opportunity Map



Implement Now

- Biobased solvents

Implement in Near Future

- Biosurfactants
- Enzymes

Research Needed

- NADES
- Oil-adhesive surfaces

Thank you