
LIVE

FOOD stars Innovative Food Product Development Cycle: Frame for Stepping Up Research Excellence of FINS

Some properties of and processes with Green Solvents

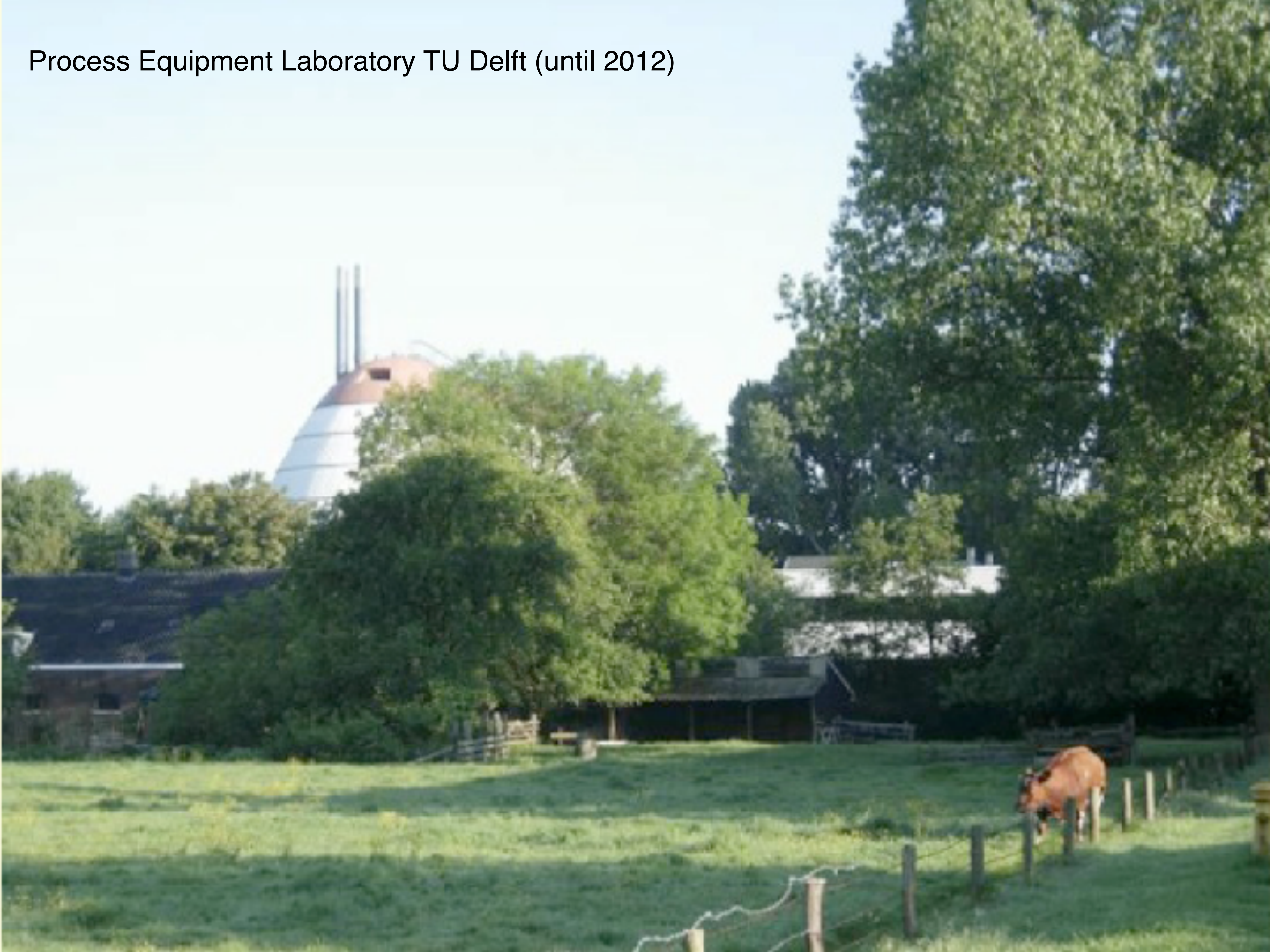
Workshop Novi Sad 27-29 May 2017

Geert-Jan Witkamp, Delft University of Technology

Green Solvents

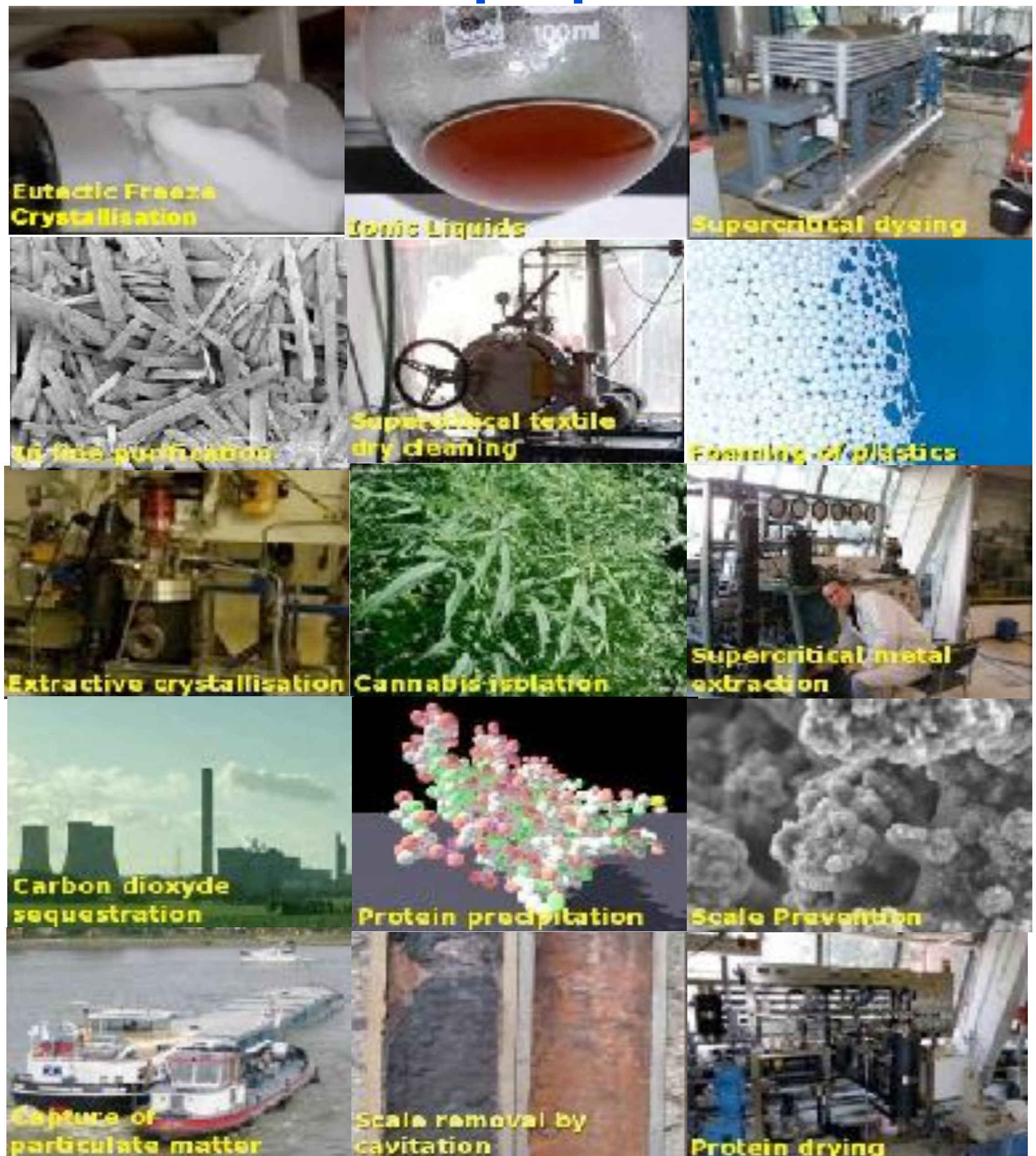
- **Supercritical carbon dioxide**
- Water
- Some Ionic Liquids
- Many Deep Eutectic Solvents (DES)
- (Virtually) all Natural Deep Eutectic Solvents (NADES)

Process Equipment Laboratory TU Delft (until 2012)

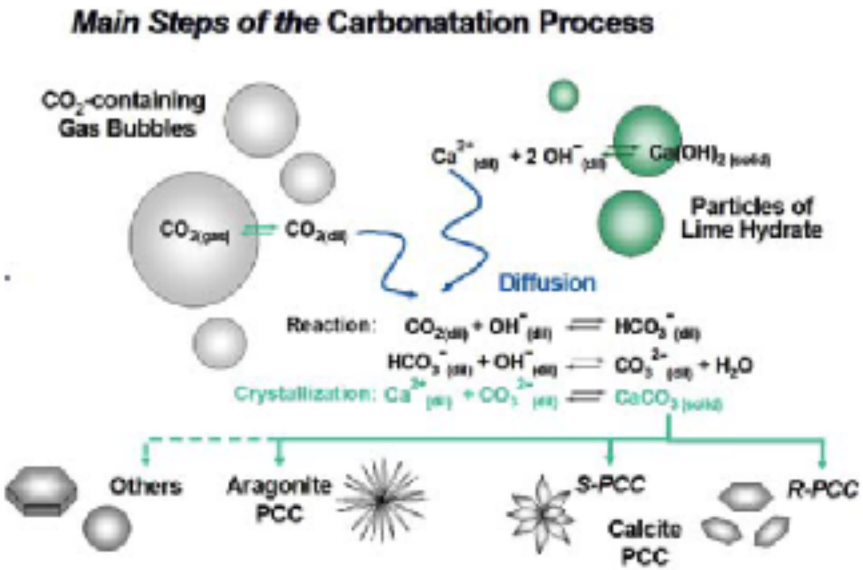


Process Equipment Delft

www.api.tudelft.nl

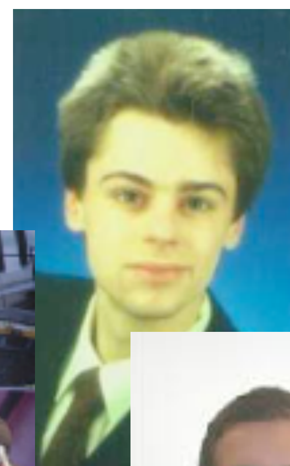


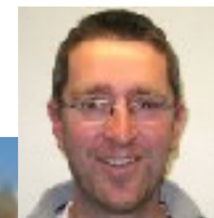
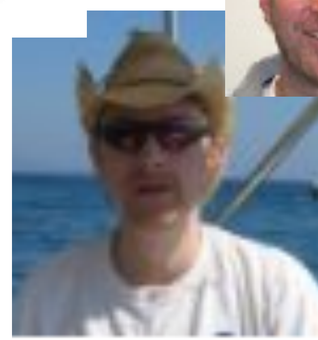
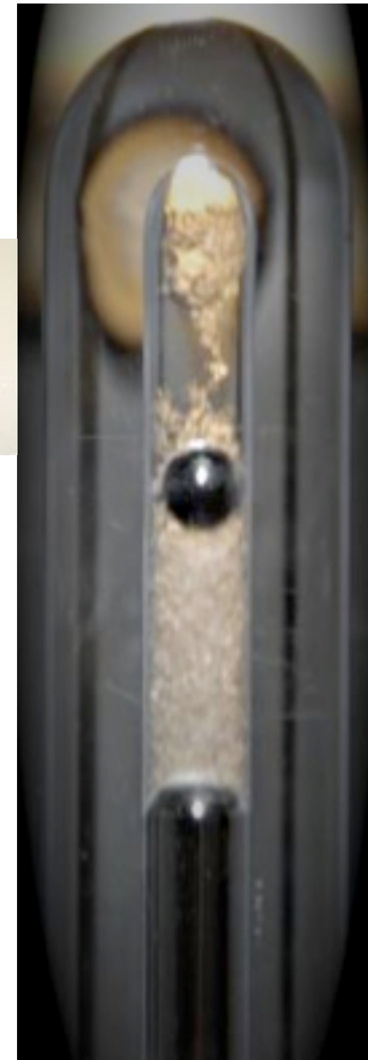
CO2/(eutectic) crystallisation

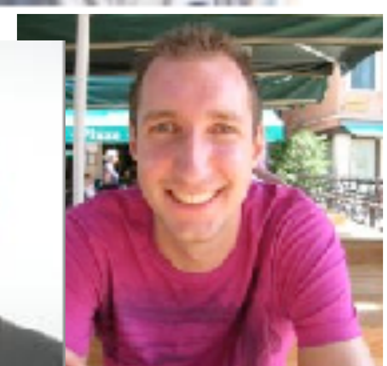


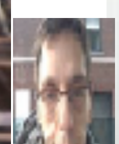






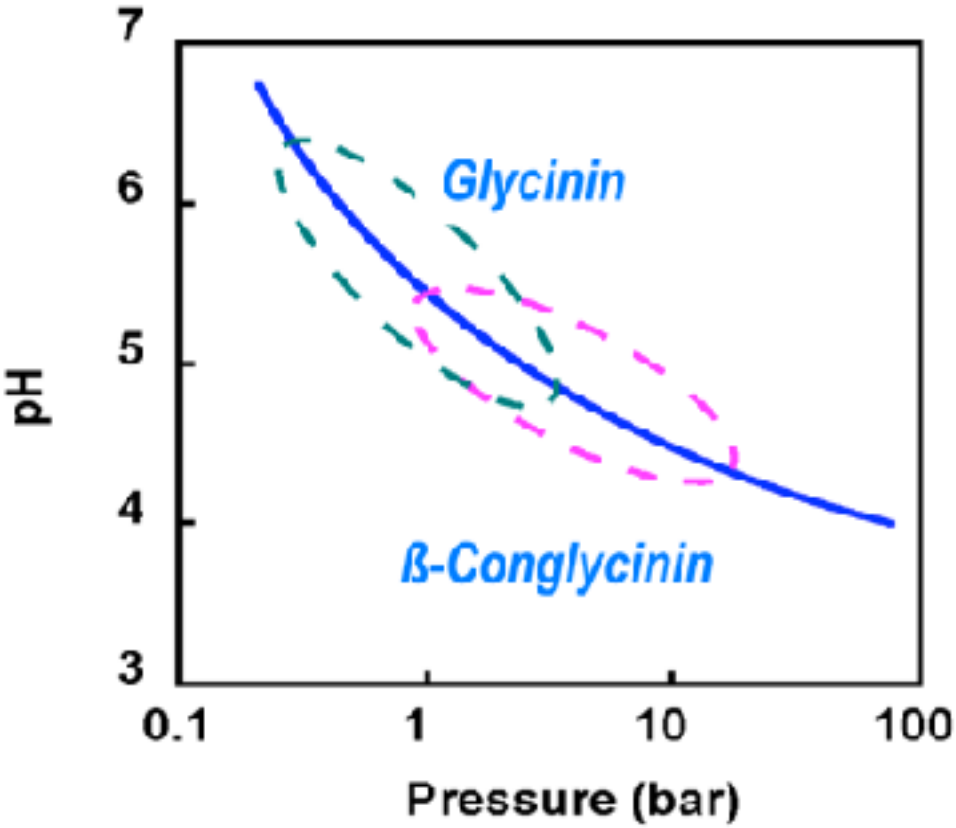




protein precipitation/formulation

CO_2 as an reversible acidifier

Principle: Use acidifying power of CO_2 to temporarily change pH of aqueous solutions, here for soy protein precipitation



Hofland et al., 2001

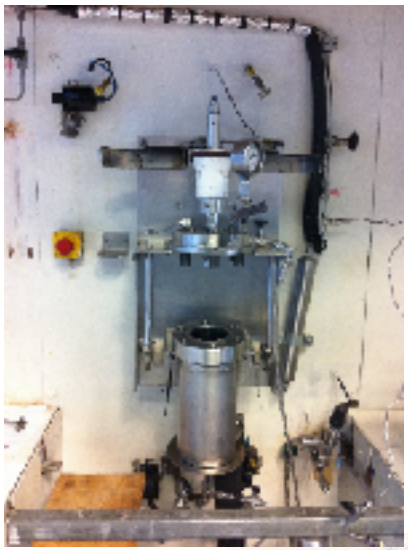
Fractionation of proteins

Gentle precipitation

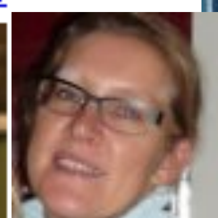
Applications CO_2 as acid

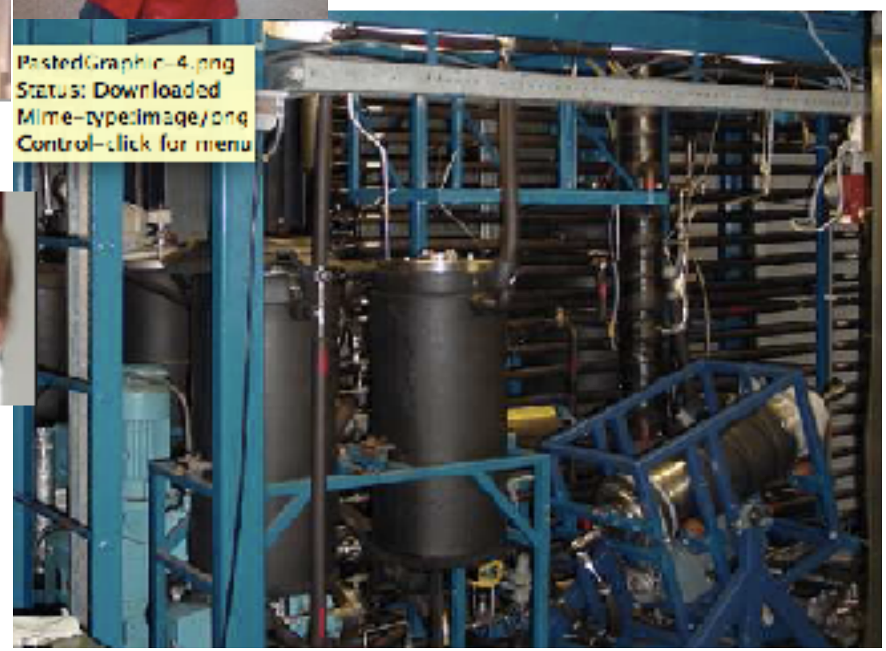
- Soy bean protein, casein (ex milk)
- Coprecipitation of enzymes (activity proven to be maintained)
- Fractionation, 98% purity of glycinin obtainable from soy at large scale (10000 times cheaper than chromatographic)

CO2/Ionic liquids



Extraction/separation/misc

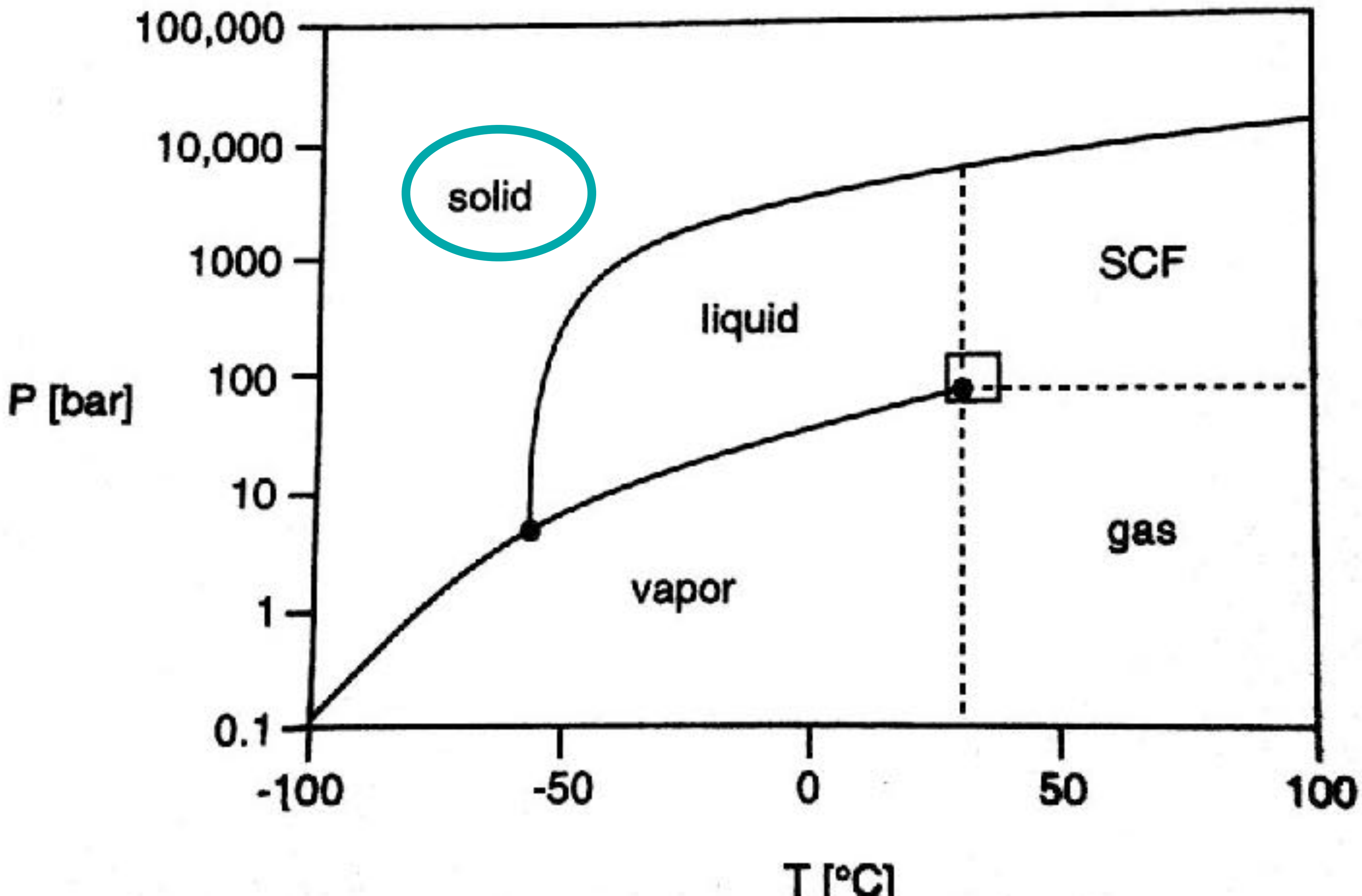




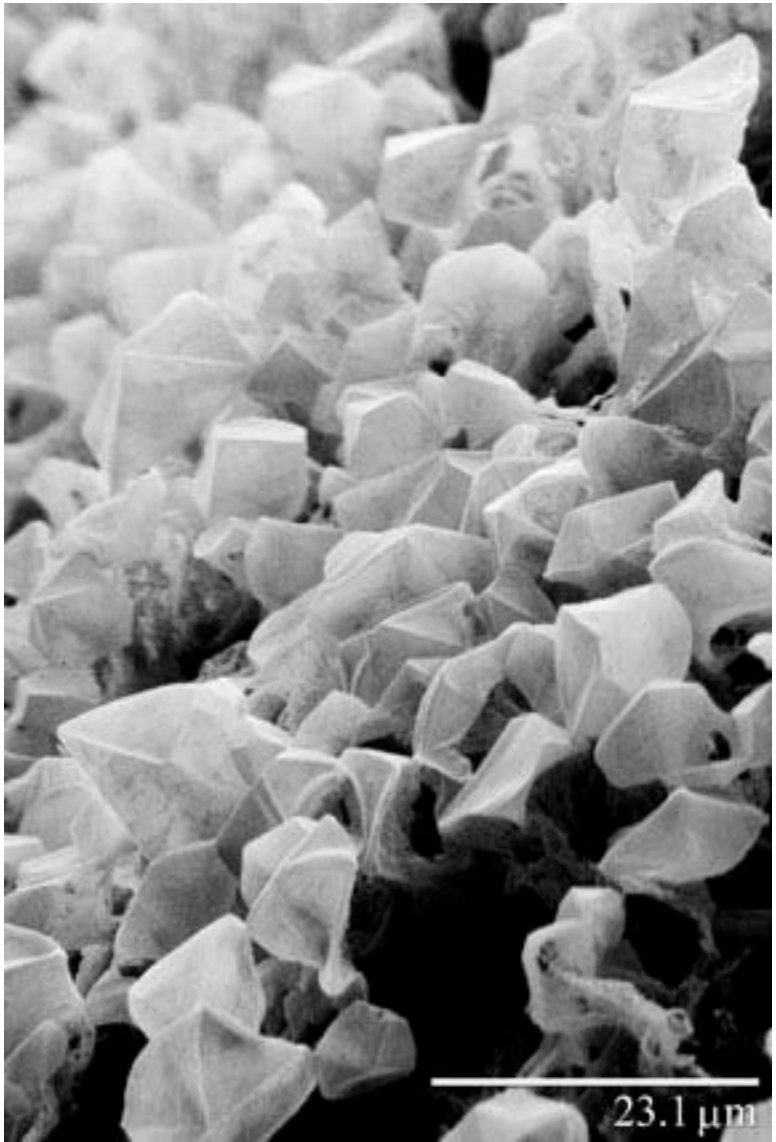
Occurrence of carbon dioxide

- On Mars: 0.01 bar CO_2, around 0 °C
- On Venus: 100 bar CO_2, 400 °C
- On Earth: 0.0004 bar, 15 °C

Phases of carbon dioxide (Jessop &Leitner)



Carbon dioxide crystals



Under pressure everything becomes solid,not liquid !

- Carbon dioxide is a solid at around -80 degrees (dry ice), but also at room temperature and ca. 3000 bar
- Also water is a solid at high pressures

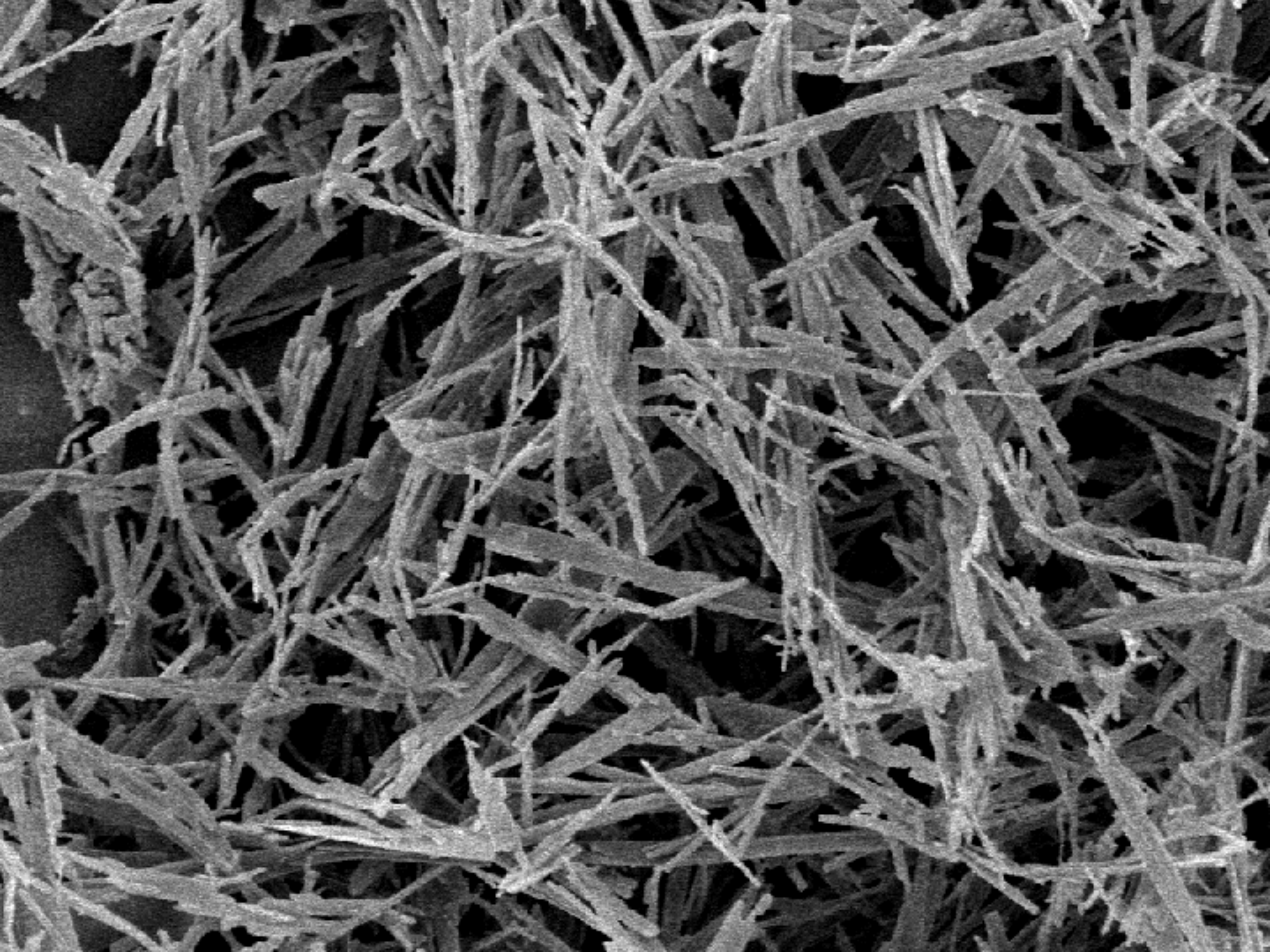
What on can we do with CO_2 ?

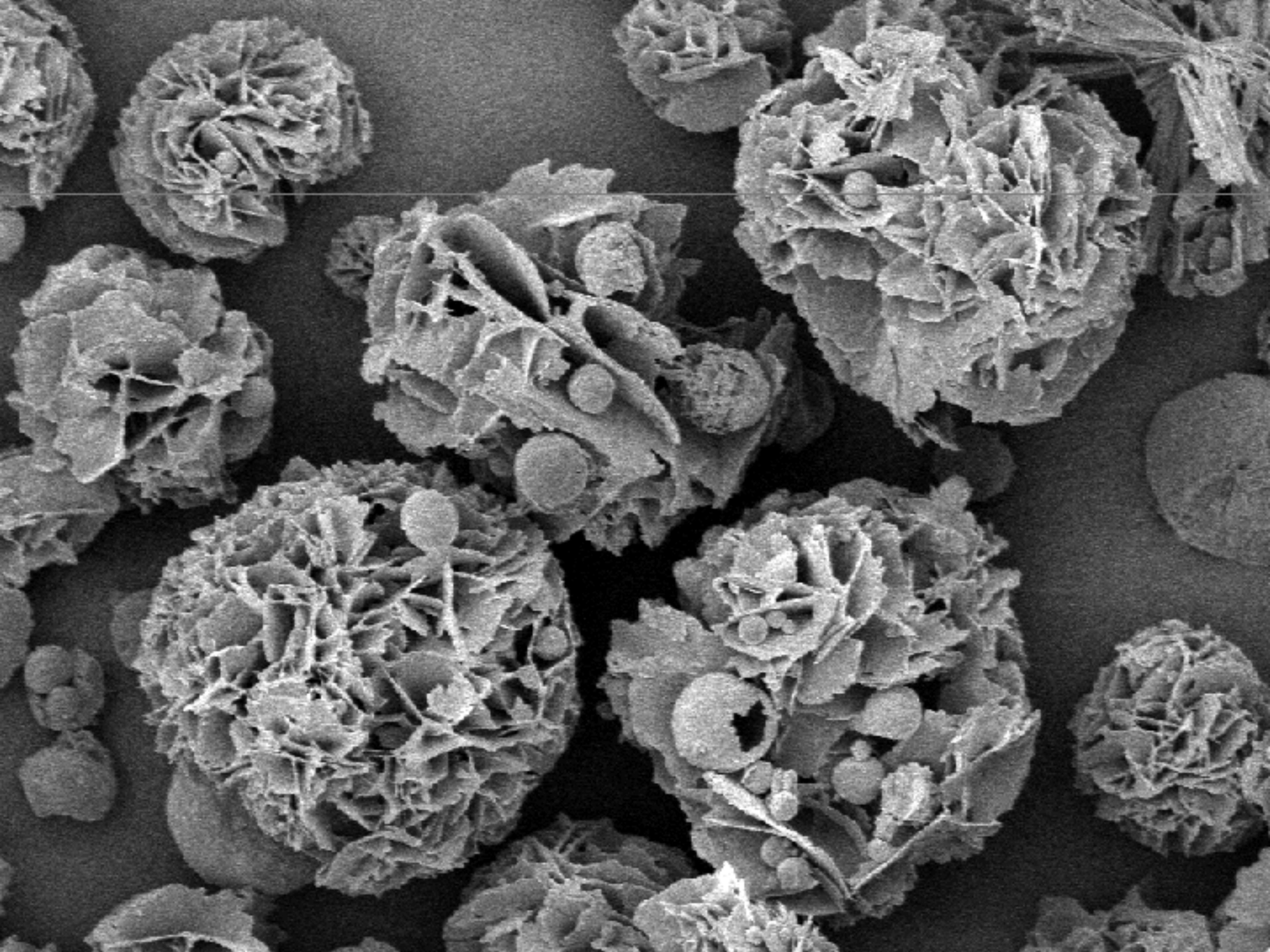
- Industrial dry cleaning: <u>no</u> organic use
- Textile dyeing:<u>no</u> 100kg H_2O/kg textile
- Extraction/crystallisation of natural materials and pharmaceuticals containing <u>no</u> solvent
- Extraction from sludges:<u>no</u> organic solvent use
- Acidify an aqueous solution, to precipitate e.g. proteins using <u>no</u> H_2SO_4
- Combine with ionic liquids: a new class of processes
- Foaming, density separation, sterilisation etc

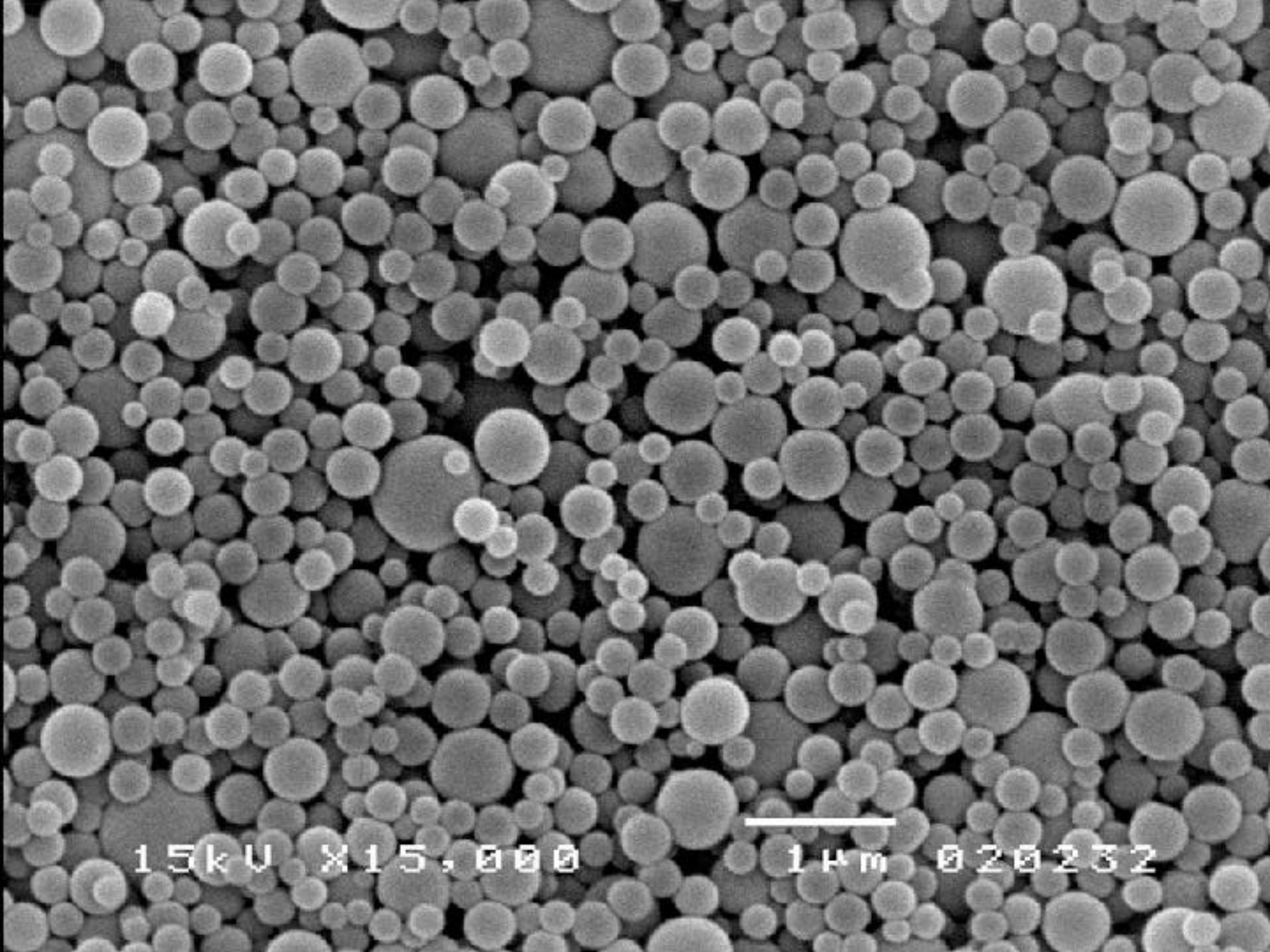
Conditions can be controlled extremely well, with the speed of sound, to give controlled expansion and compression (SESS)

Piazzolla.org

Less well controlled expansion with speed of sound (RESS)



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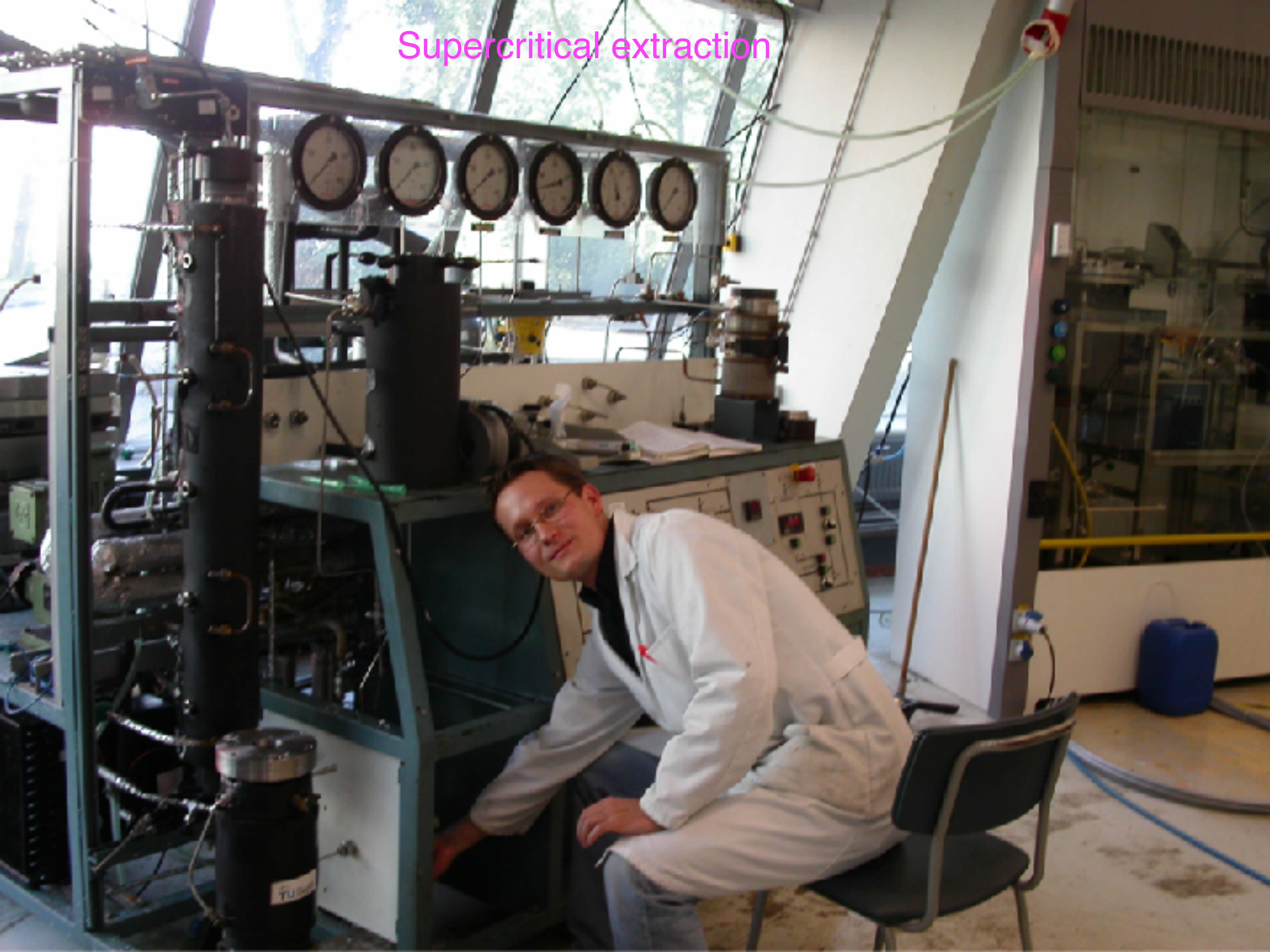
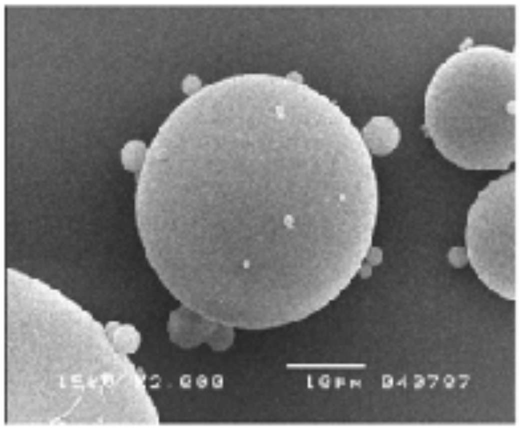
Supercritical extraction

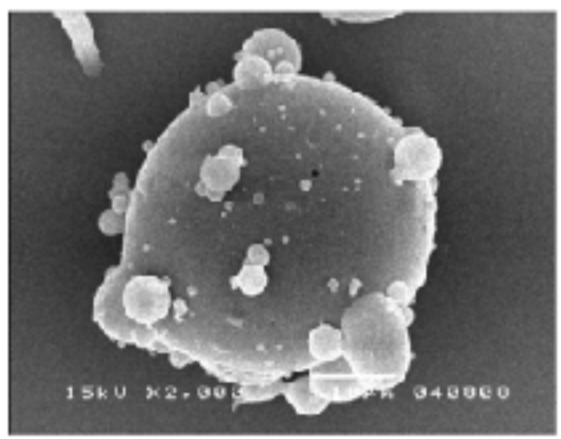


Melt micronised hydrogenated castor oil (dissertation Munuklu)



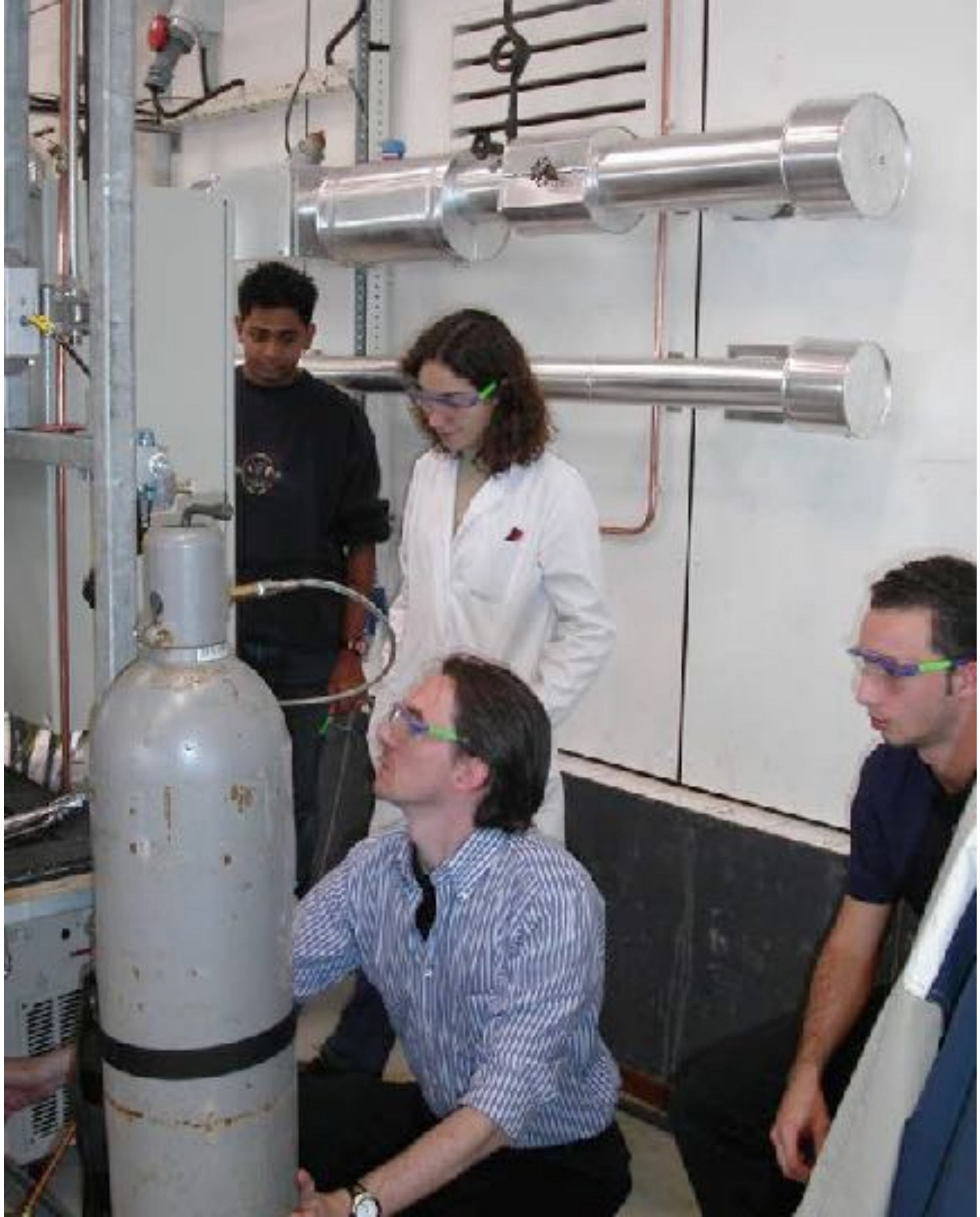
a)

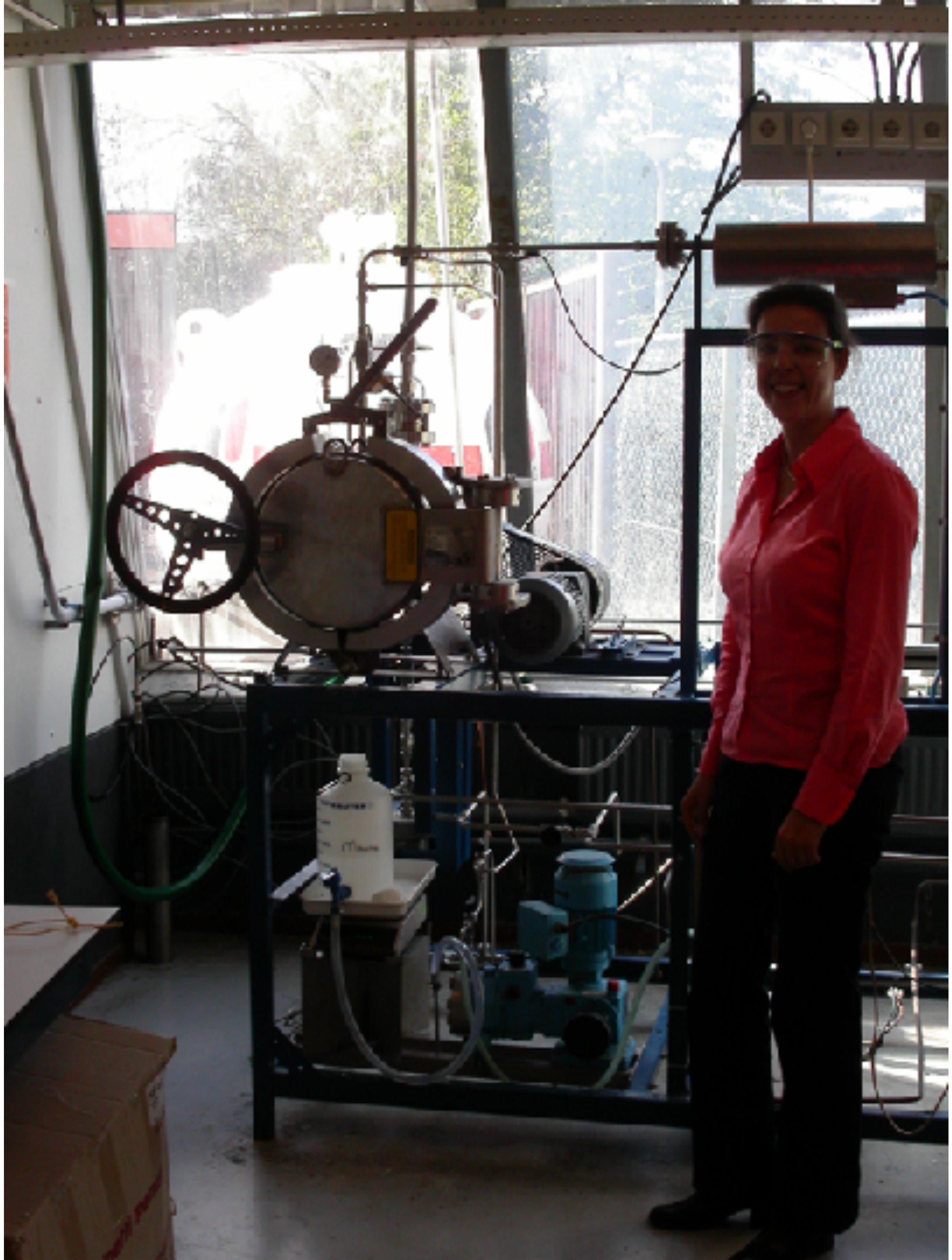
b)



c)

Figure 2: SEM-pictures of the HCO results at constant pressure and temperature (150 bar / 100°C) a) 5, b) 10, c) 20 wt%.





Where to get CO_2, at what price ?

- CO_2 is formed in huge amounts in energy and process industry, in very pure form in fertiliser industry
- Costs about 10 cent per kg,
- Compression costs

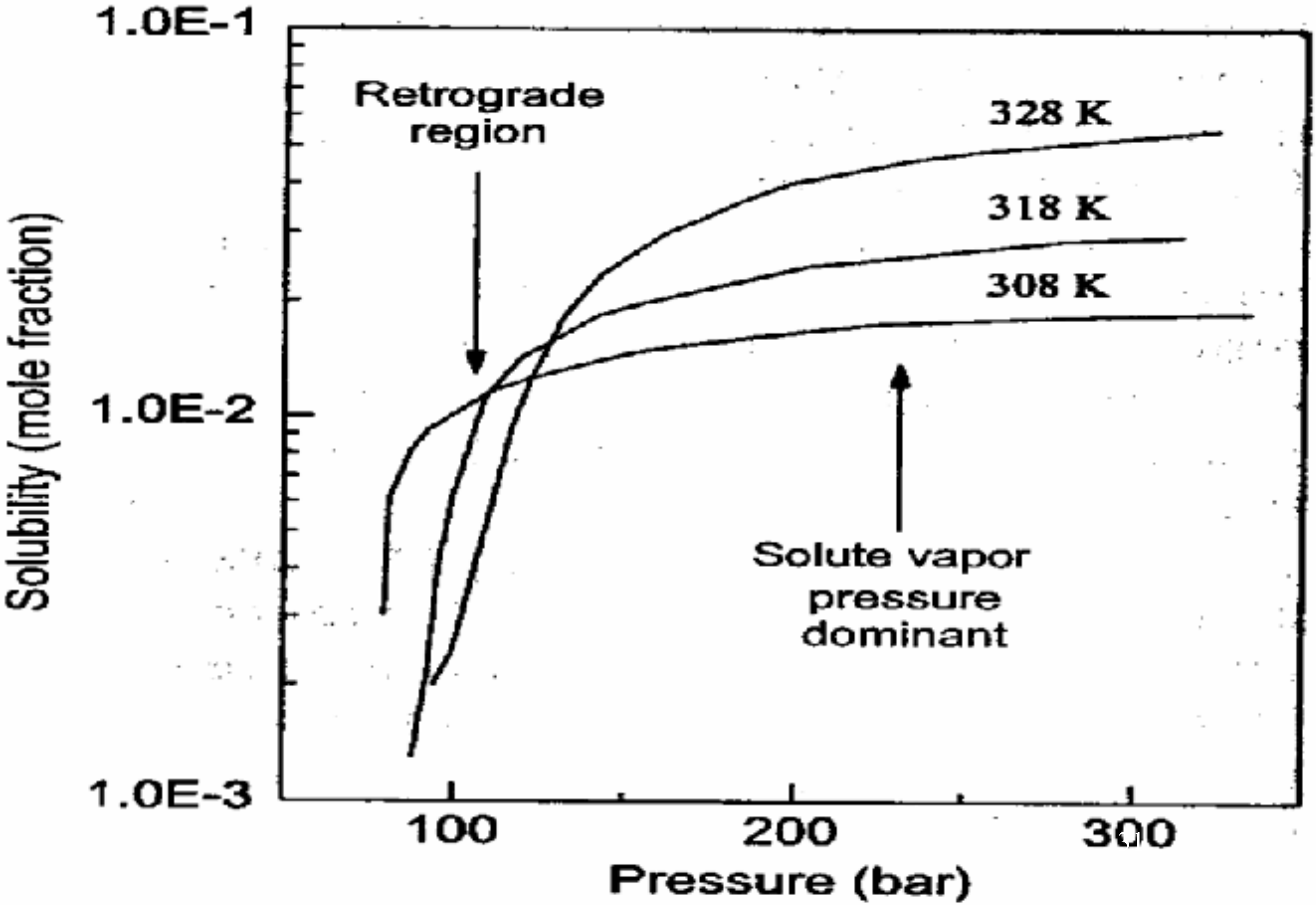
Are pressurised processes expensive ?

Polyethylene: 3000 bar, flammable, in a 3 km pipe reactor, velocities up to 100 m/s, yield is 30% only per pass. Nevertheless, added value less than 100 euro/ton.

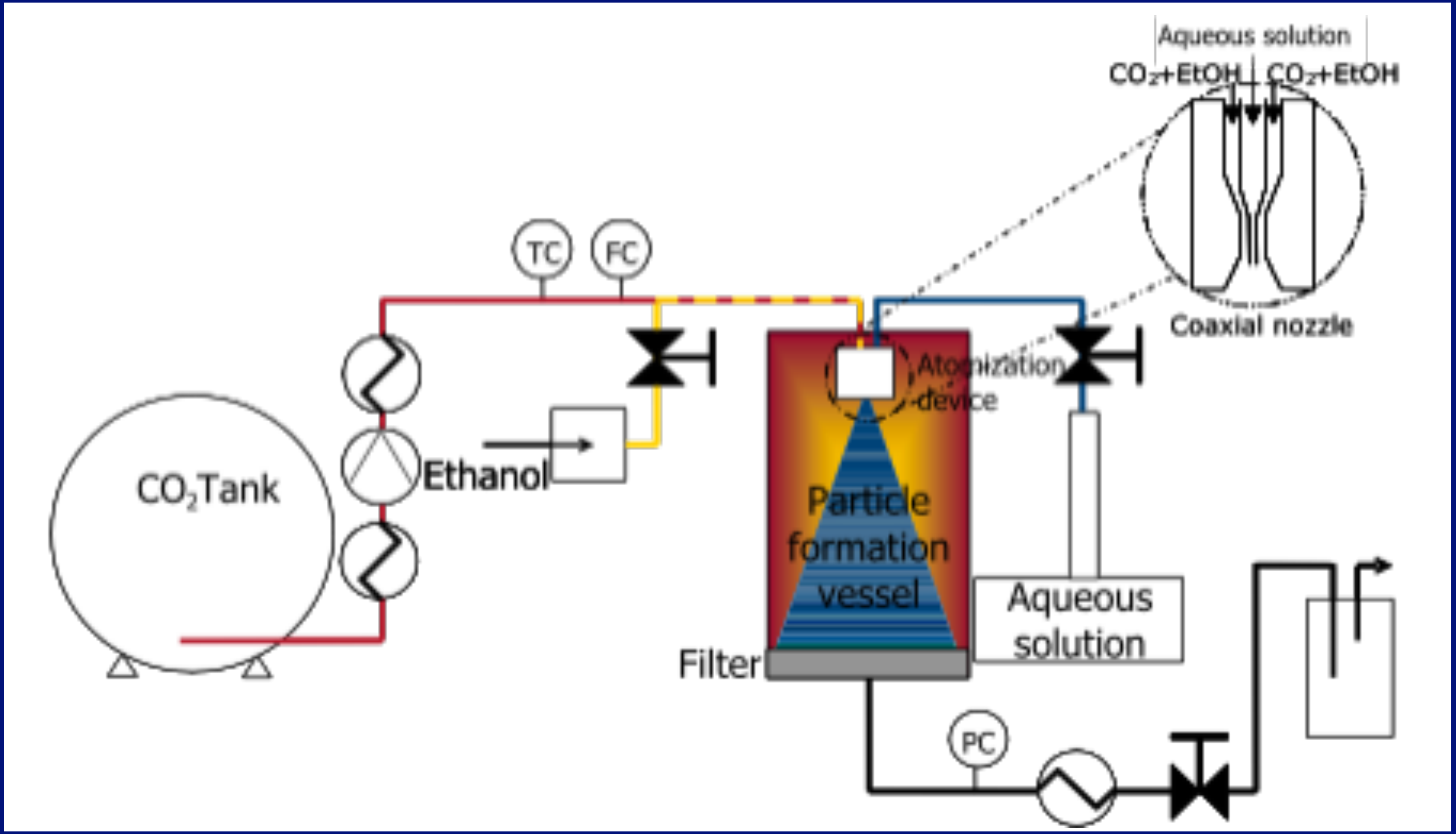
→

High pressure based processes, in particular those using CO_2, are expected to cost around 0.1 to 1 euro per kg treated product.

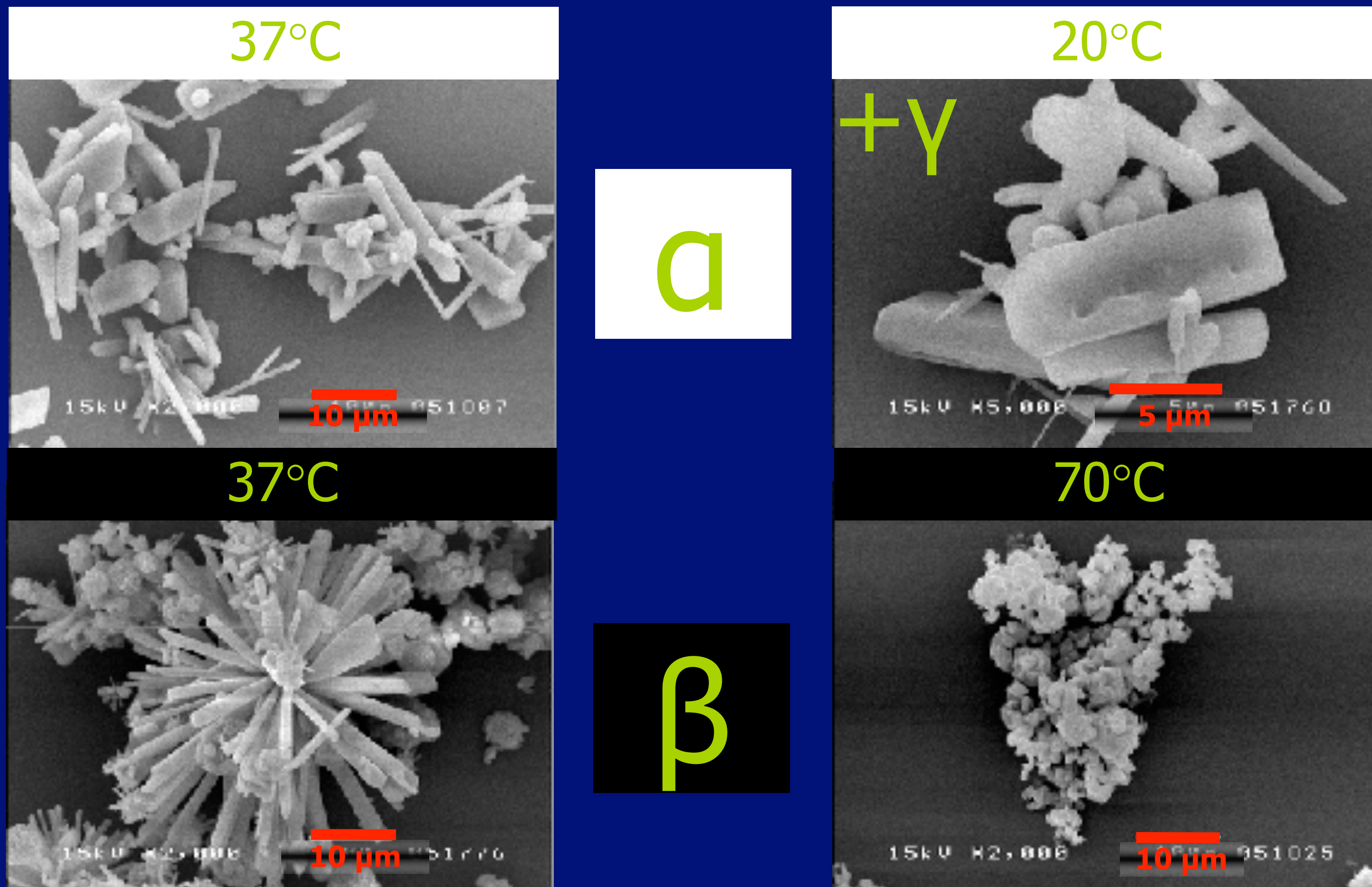
NAPHTALENE SOLUBILITY IN CO2(Jessop/Leitner)



SCF-drying equipment



Drying of compounds with CO2
Glycine morphology – Temperature



Textile dry-cleaning/textile dyeing

Comparison textile dyeing methods

	Conventional Process	With $scCO_2$
Clean water use	100 L/kg textile	0
Waste water	100 L/kg textile	0
Dye loss	up to 50%	no
CO_2 emission	0.7 kg/kg product	0.5 kg/kg product
Production rate	300 kg/2 hr in a 1000L machine	300 kg in 1 hr
Costs	1 euro/kg product	0.5 euro/kg product

By **Sustainable Business News**
Published December 17, 2013
Tags: Chemicals, Supply Chain, More...

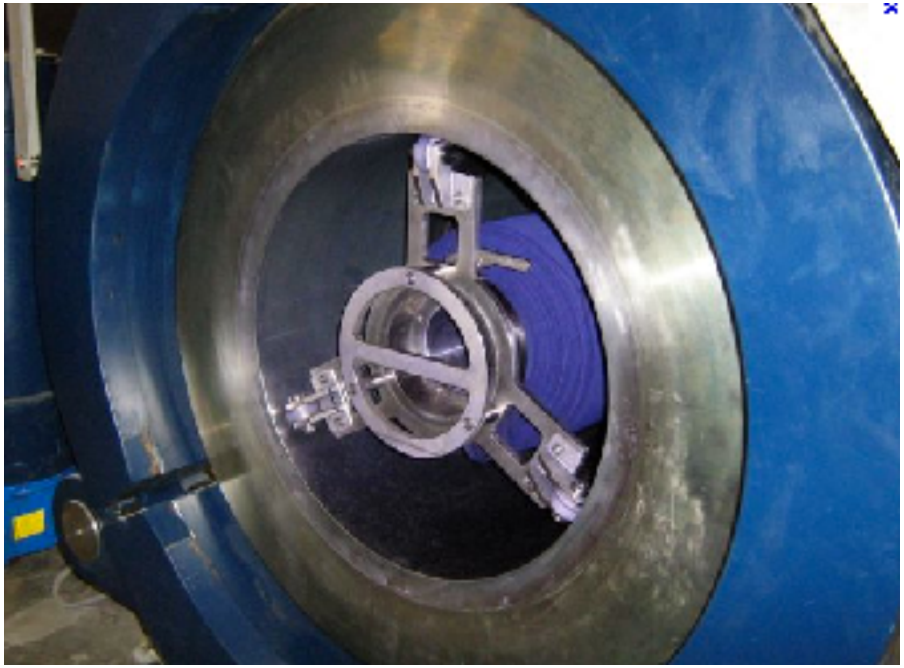
Email | Print | Single Page V

Nike and Adidas are beginning to use what they call a "revolutionary technology" for the textile industry — a carbon-based process that dyes polyester without the use of water or chemicals.

The technology, Nike says, can revolutionize tex manufacturing, whose toxic footprint comes mos from dyeing and which relies on enormous amounts of water.

"We want to collaborate with progressive dye houses, textile manufacturers and consumer apparel brands to scale this technology and pus throughout the industry," says Eric Sprunk, Nike

First full scale machines operating in Thailand



FEBRUARY 07, 2012

NIKE, INC. ANNOUNCES STRATEGIC PARTNERSHIP TO SCALE WATERLESS DYEING TECHNOLOGY

The company has entered into a strategic partnership with DyeCoo Textile Systems B.V., a Netherlands-based company that has developed and built the first commercially available waterless textile dyeing machines.

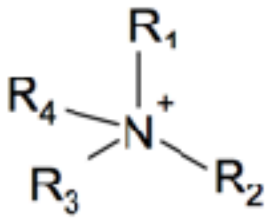
Green Solvents

- Supercritical carbon dioxide
- **Some Ionic Liquids**
- Water
- Many Deep eutectic Solvents (DES)
- (Virtually) all Natural Deep Eutectic Solvents (NADES)

Ionic Liquids

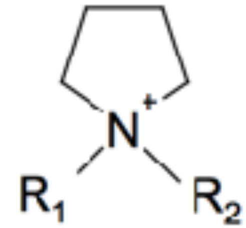
- Solutions made from ions (salts that are liquid at room temperature), Organic or organic-inorganic combinations
- Very low vapour pressure (separate ions do not evaporate, ion pairs are not strong enough).
- Can be green if constituents are green.
- Can be hydrophobic or hydrophilic.
- Mostly mainly electrostatic bonding.
- Solvent for chemical or enzymatic reactions, for extraction of (bio-)materials

Common cations:

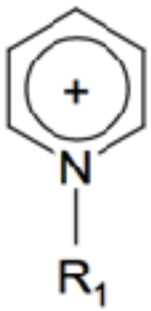


Ammonium

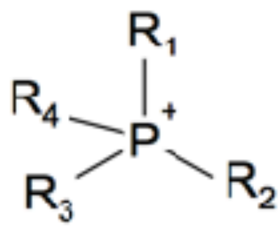
Imidazolium



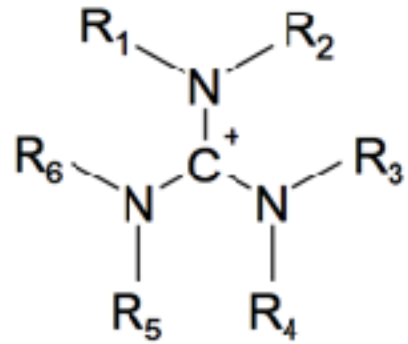
Pyrrolidinium



Pyridinium



Phosphonium



Guanidinium

Common anions:

Chloride: Cl^-
Methylsulfate: $CH_3OSO_3^-$
Triflate: $CF_3SO_3^-$
Trifluoroacetate: $CF_3CO_2^-$
Hexafluorophosphate: PF_6^-
Tetrafluoroborate: BF_4^-
Bis(trifluoromethanesulfonyl)imide: $N(CF_3SO_2)_2^-$
Dicyanamide: $N(CN)_2^-$

Figure 2.1: Most common cations and anions[10]

Solubility of CO2 in Ionic Liquids is high

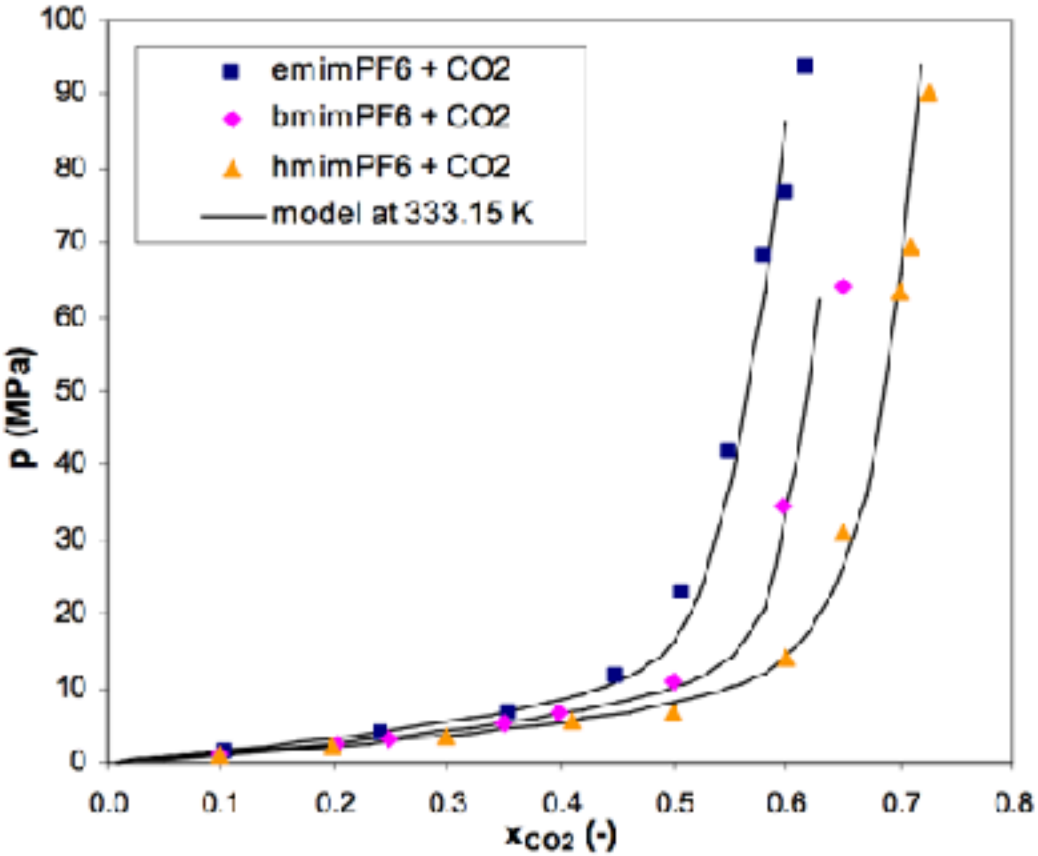


Figure 6.3: Experimental data[12,13,16] and tPC-PSAFT equation of state correlation for the bubble-point pressures of different ionic liquid (anion = PF_6^-) + carbon dioxide systems at 333.15 K

Ionic Liquid-scCO2 combinations

- First reaction, or extraction using IL or a scCO2/IL combination (single phase). Subsequently at a different pressure:
- CO2 can be applied to extract product from IL
- or CO2 can be used as antisolvent, causing product to fall out.

Deep eutectic solvents

- Mixtures of solids that form a liquid at room temperature or below.
- Constituents can be ions (then ionic liquid), neutral molecules (urea) or combinations.

What is a Eutectic ?

from the Greek "ευ" (eu = easy, well) and "Τήξις" (teksis = melting).

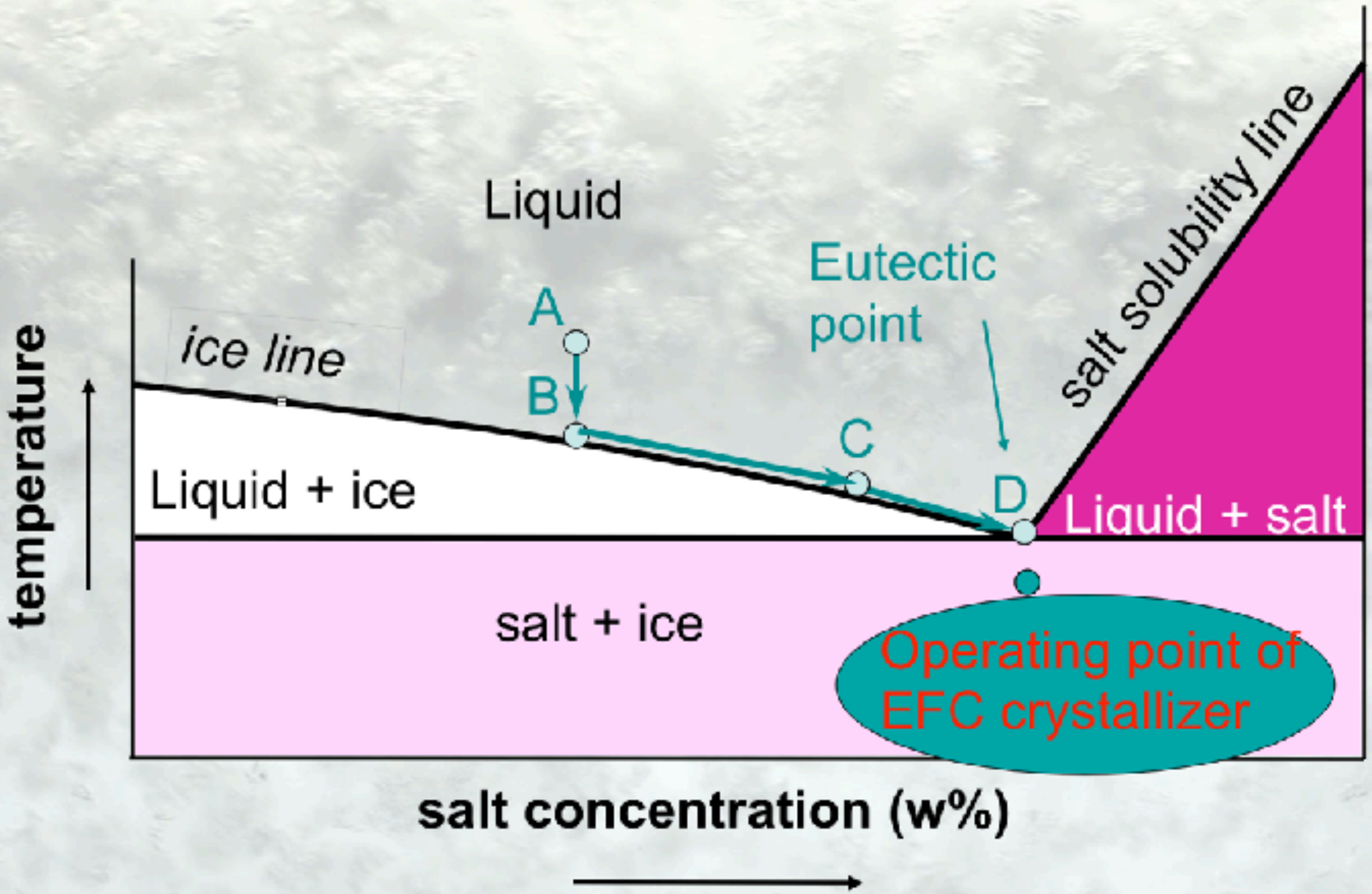
Green Solvents

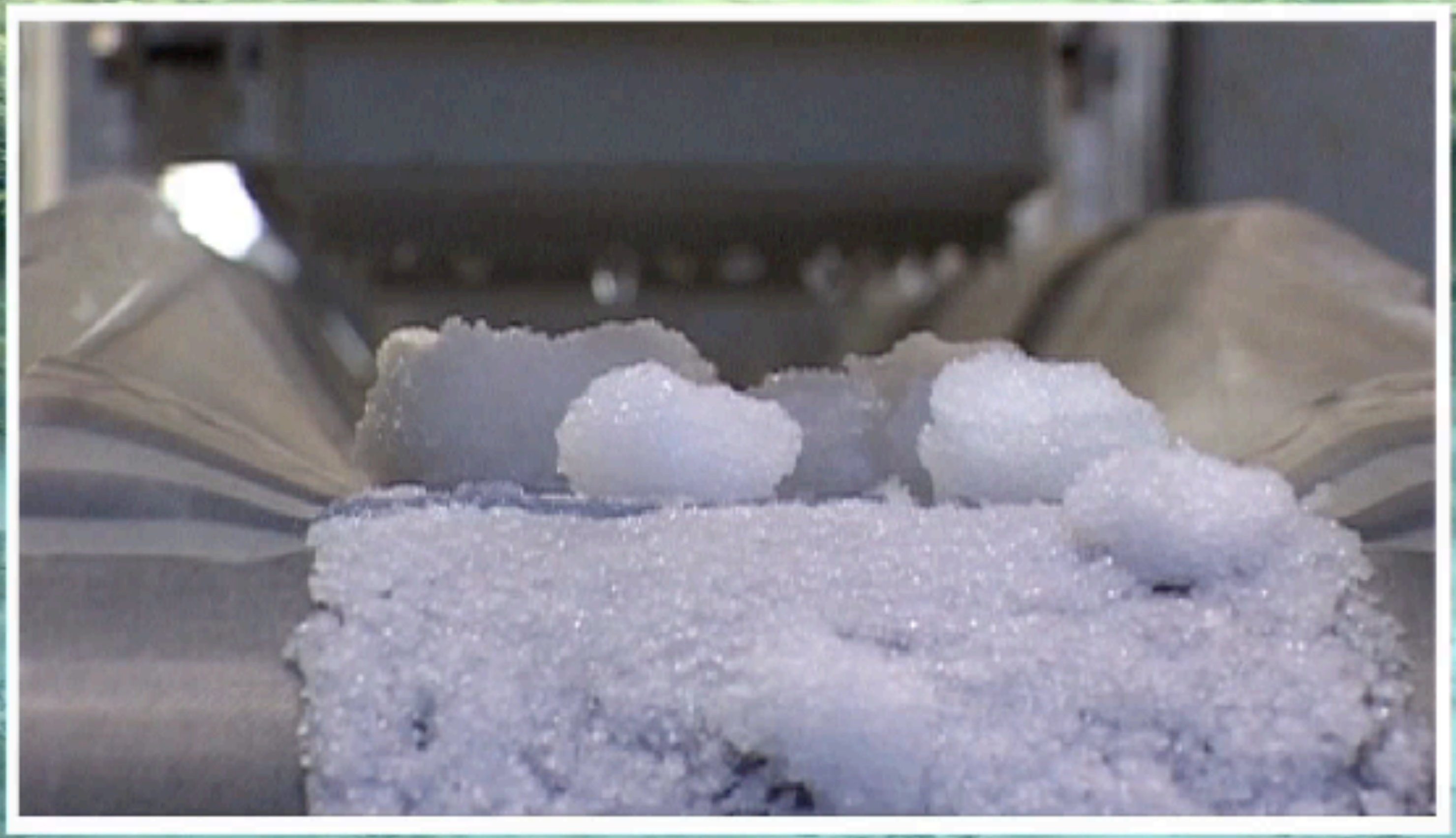
- Supercritical carbon dioxide
- **Water**
- Some Ionic Liquids
- Many Deep eutectic Solvents (DES)
- (Virtually) all Natural Deep Eutectic Solvents (NADES)

Geert-Jan Witkamp

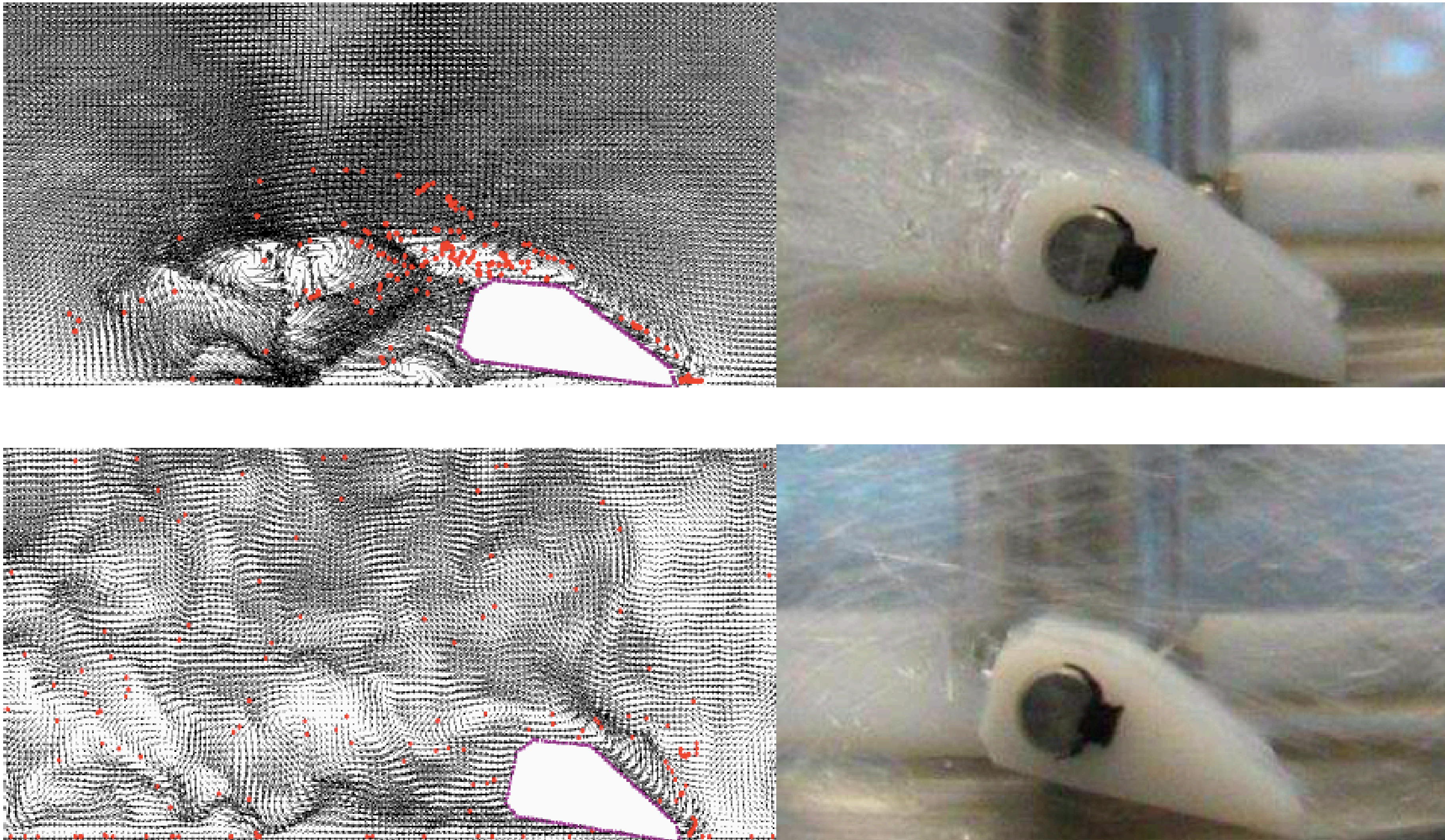
Eutectic: example eutectic freeze crystallisation

Application:
Crystallisation of highly pure materials from aqueous solution.
Salts, acetic acid, glucose.


Liquid
Eutectic point
salt solubility line
A
B
C
D
ice line
temperature
Liquid + ice
Liquid + salt
salt + ice
Operating point of EFC crystallizer
salt concentration (w%)

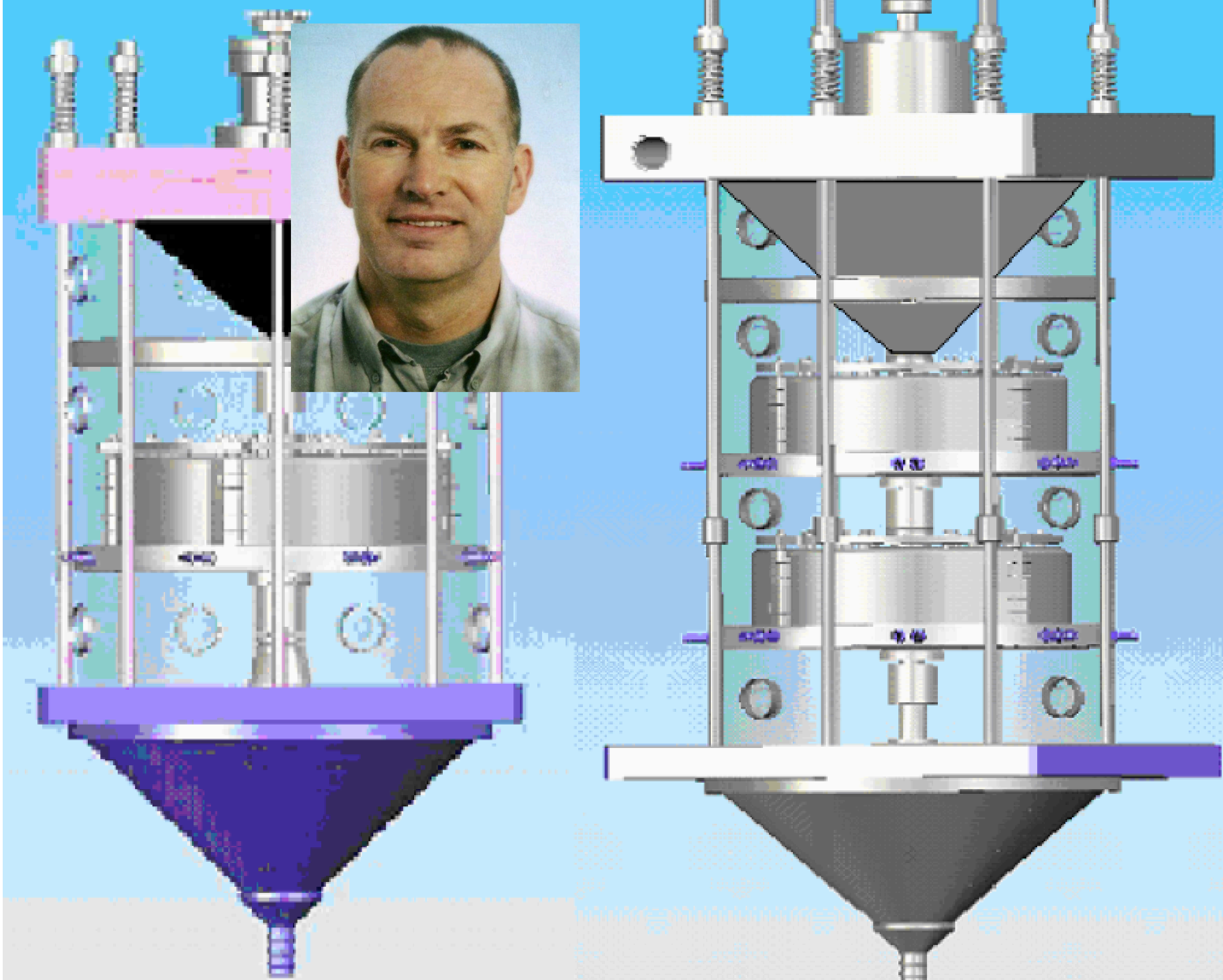


Evelien Pingen best MSc TUD 2008/9



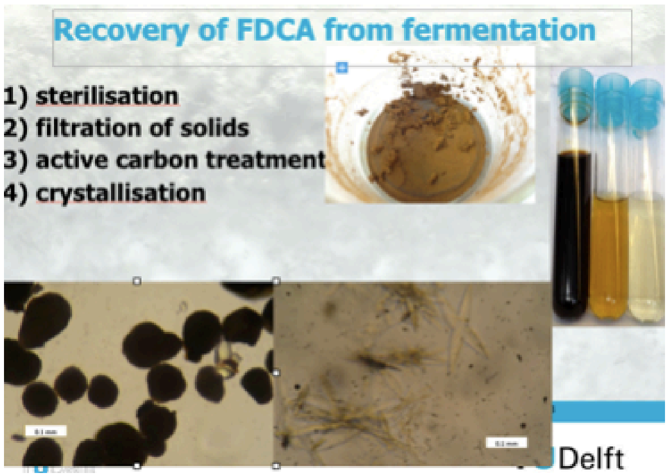
from Marcos Rodriguez, PhD thesis

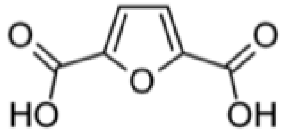
Figure 6. *Particle trajectories from particle-flow simulations for the streamlined scraper geometry compared to measured particle-flow visualization. The top two figures correspond to 20 seconds after start up, and the bottom two to 230*



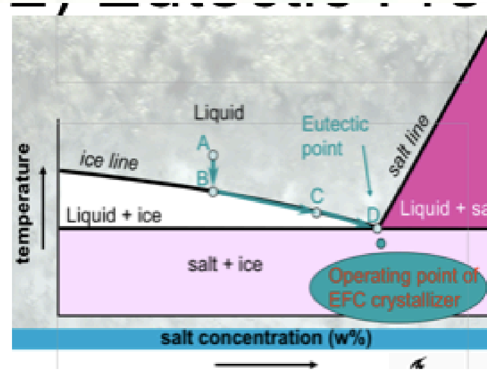
Eutectic Freezing of soda at AVR Rotterdam

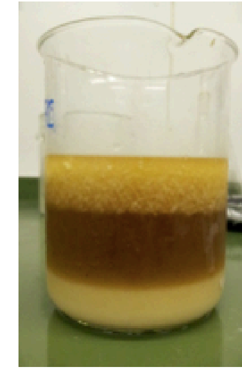
by Bird Engineering) by sterilisation, filtration, centrifugation, active carbon decolouring, crystallisation by gentle acidification or by Eutectic Freeze Crystallisation

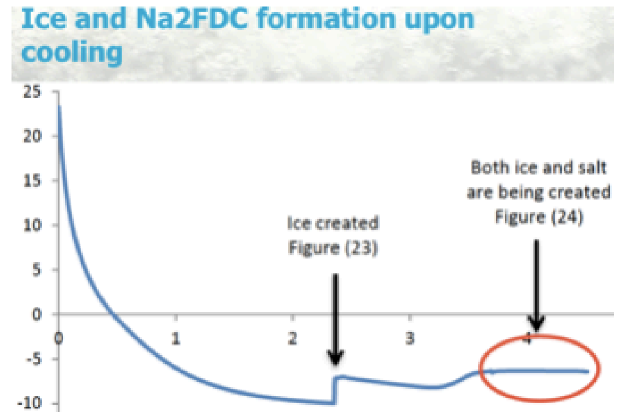


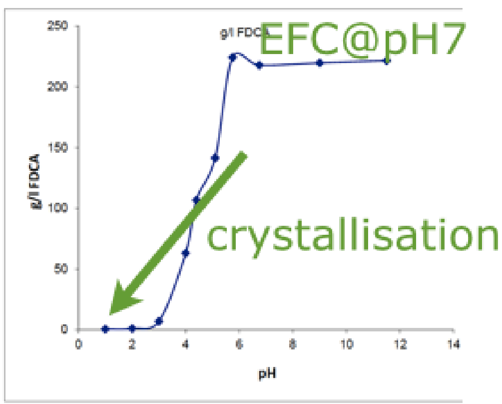


FDCA

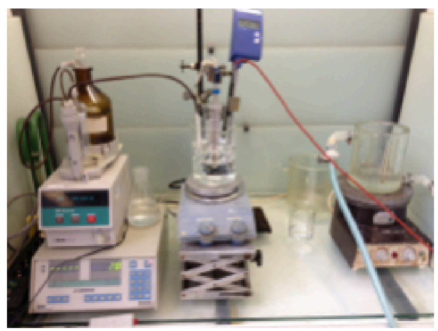








igure 3. Solubility curve of FDCA at 25°C at different pH controlled by N Wierckx, 2011)



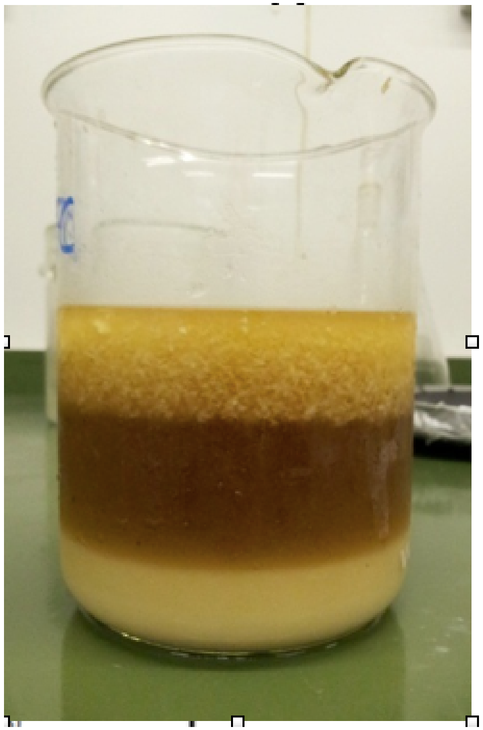
pKa = 2.6 and 3.6 resp. , under fermentation conditions (pH 7) FDCA is fully dissociated.

No HMF (-acid or - alcohol) was found in the crystals. More complete impurity profiles need to be determined.

BE-Basic

TUDelft

BEBasic project FDCA



Humic acids separation

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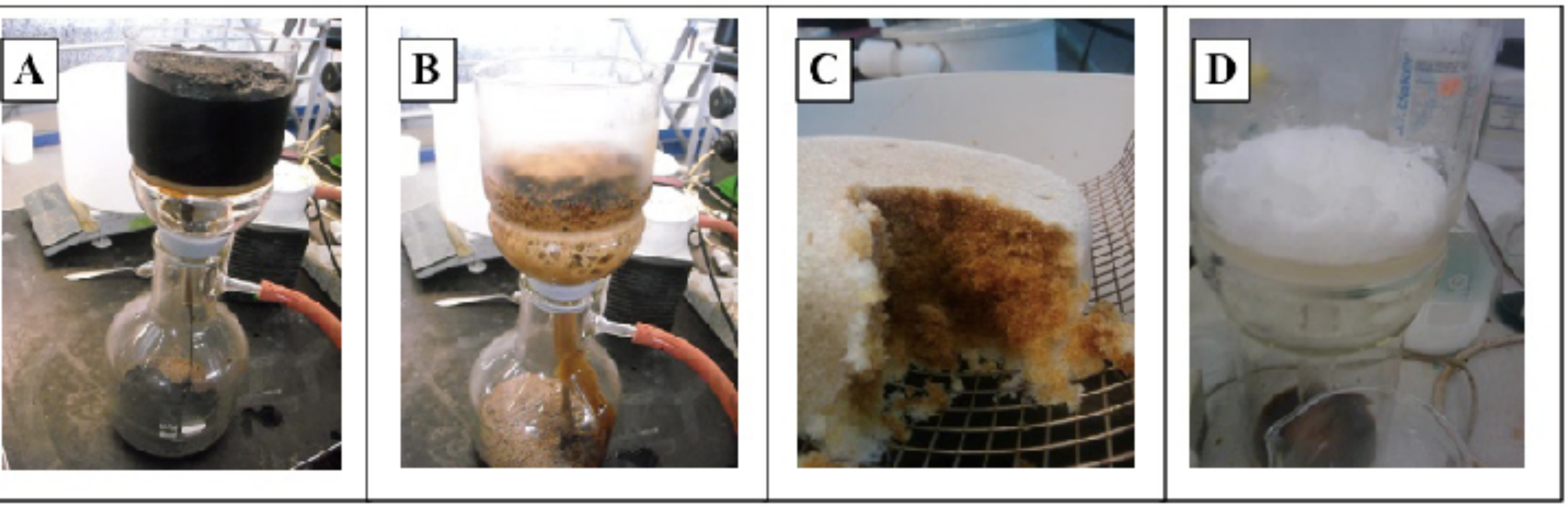
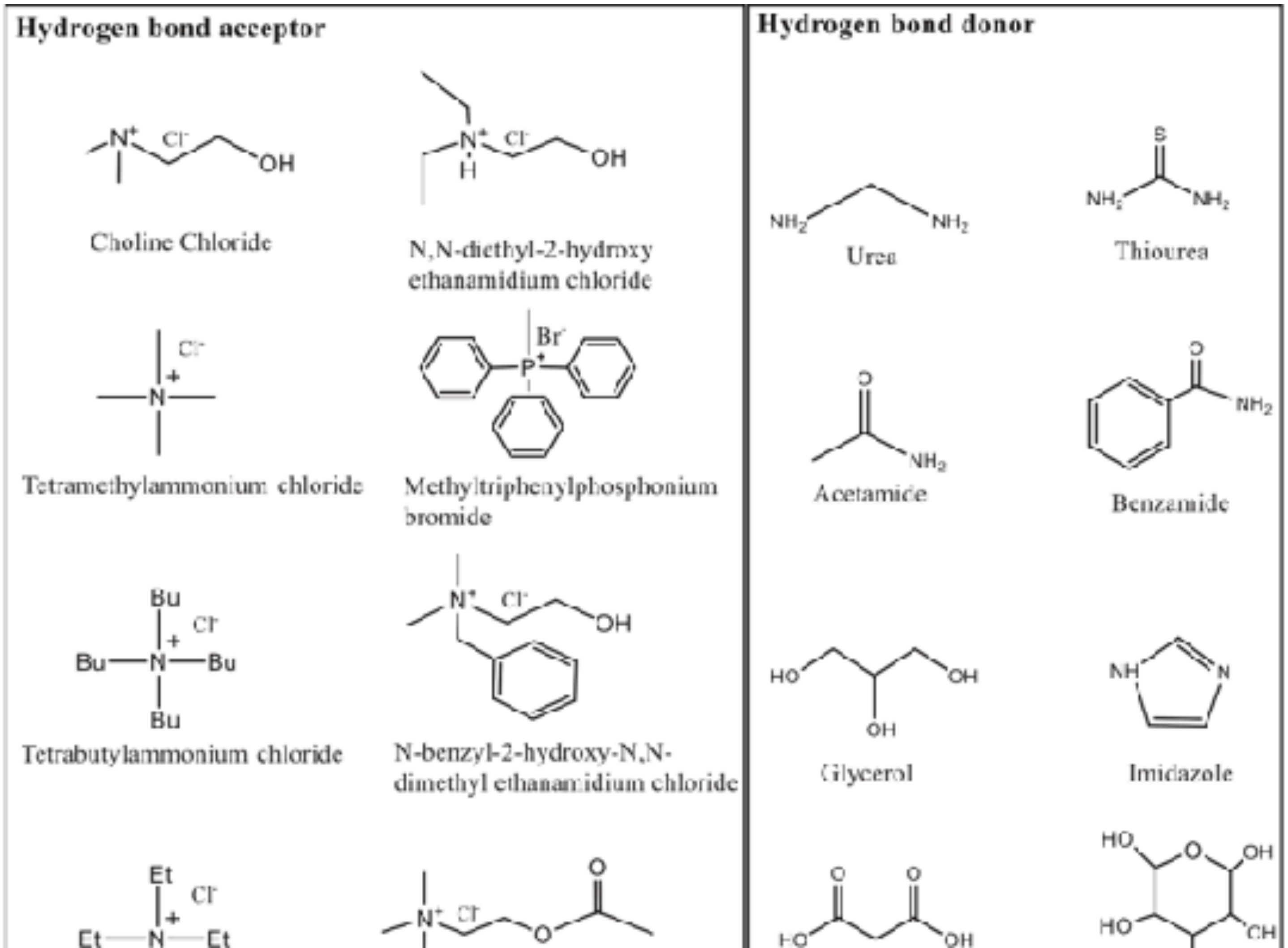
Purity of ice (from anion IX regenerate, with washing steps)



Deep Eutectic Solvents

(Q. Zhang et al, Chem. Soc. Rev., 2012, 41, 7108–7146



Green Solvents

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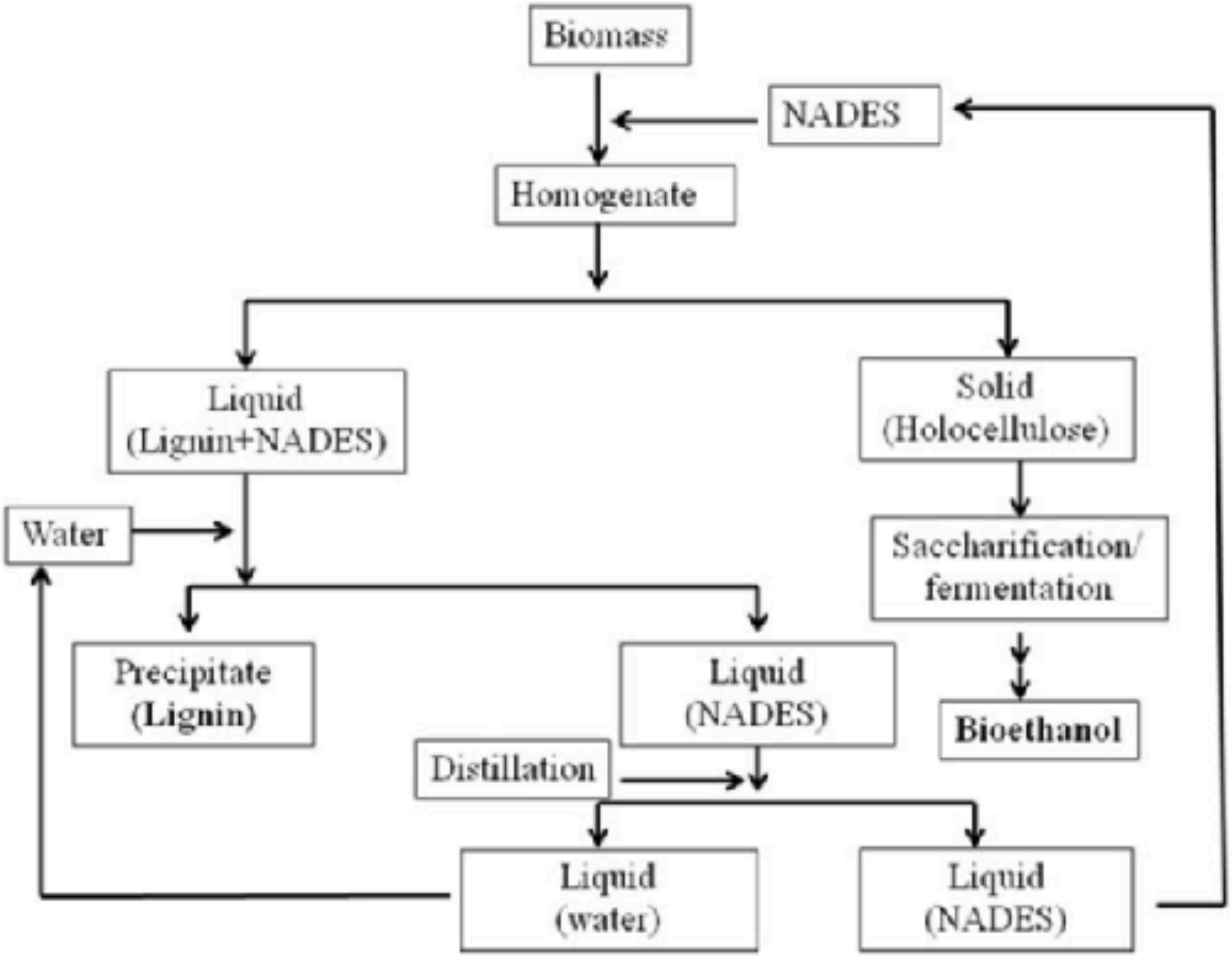
- **(Virtually) all Natural Deep Eutectic Solvents (NADES)**

Pretreatment of rice straw

Kumar et al, Envir. Sci. Pollut. Res. 23 (2016) 9265



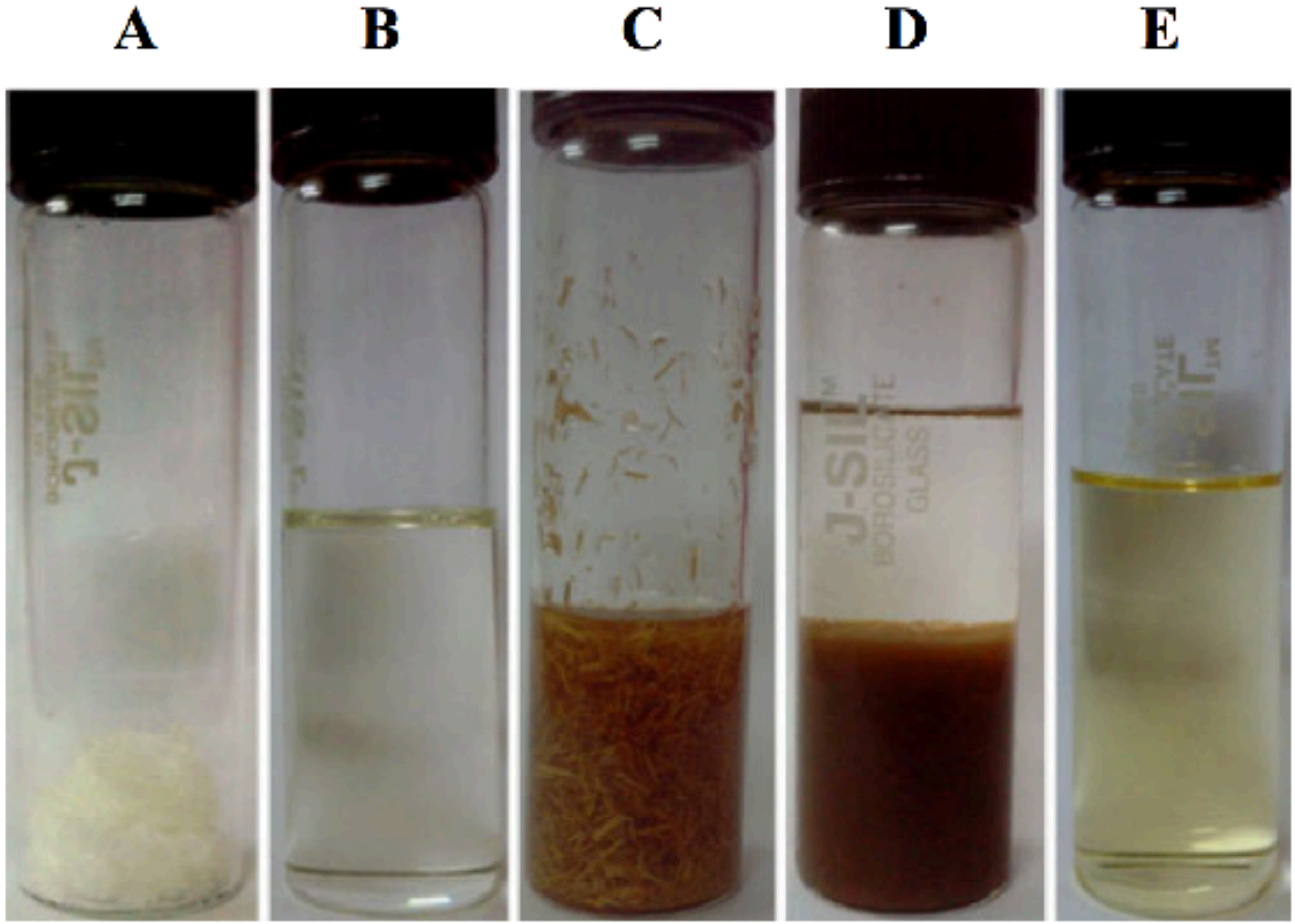
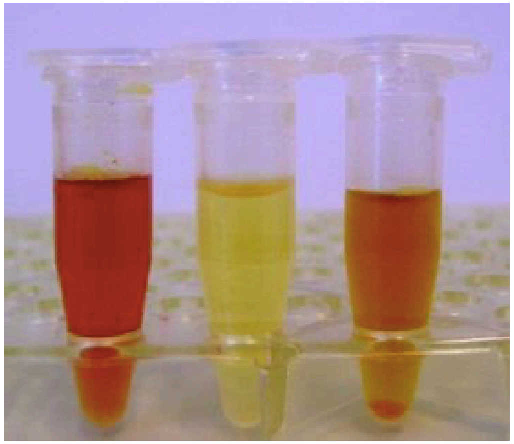


Fig. 2 Experimental demonstration of the process steps involved in NADES preparation, biomass pretreatment, and recovery. **a** NADES components before reagent preparation; **b** NADES reagent after preparation; **c** NADES-pretreated rice straw; **d** Lignin precipitate; and **e** recovered NADES reagent

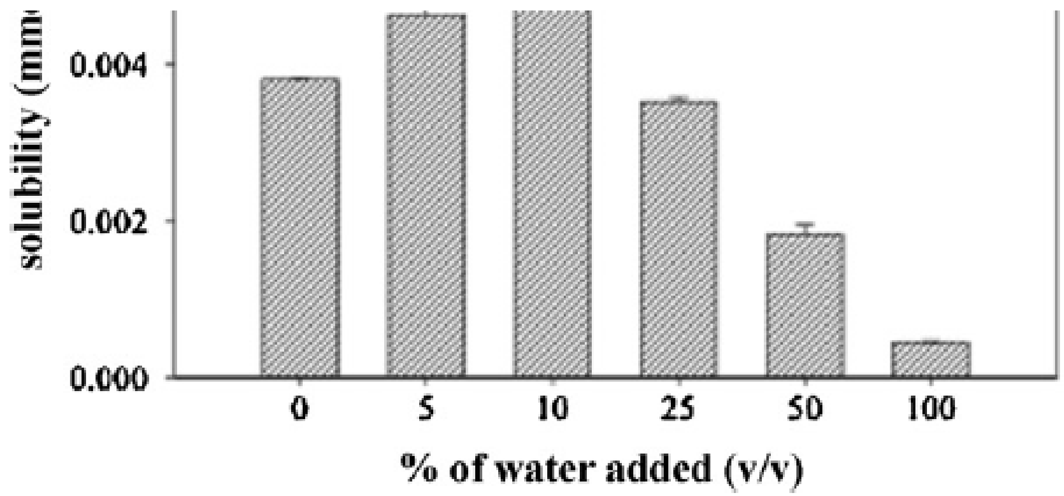
3.1 Comparison of the extractability of safflower polyphenols with NADES, water and ethanol

a)



4 2 10

b)



ig. 3. Solubility of rutin, quercetin, cinnamic acid and carthamin in glucose–choline hloride–water (2:5:5, molar ratio) diluted with different percentage of water.

Natural Deep Eutectic Solvents NADES)

Plant Physiol. Vol. 156, 2011

Are Natural Deep Eutectic Solvents the Missing Link in Understanding Cellular Metabolism and Physiology?[W]

Young Hae Choi[1], Jaap van Spronsen[1], Yuntao Dai, Marianne Verberne, Frank Hollmann, Isabel W.C.E. Arends, Geert-Jan Witkamp, and Robert Verpoorte*

Natural Products Laboratory, Institute of Biology (Y.H.C., Y.D., M.V., R.V.), Leiden University, 2300 RA Leiden, The Netherlands; and Laboratory for Process Equipment (Y.H.C., J.v.S., G.-J.W.) and Biocatalysis and Organic Chemistry Group, Department of Biotechnology (F.H., I.W.C.E.A.), Delft University of Technology, 2628 CA Delft, The Netherlands

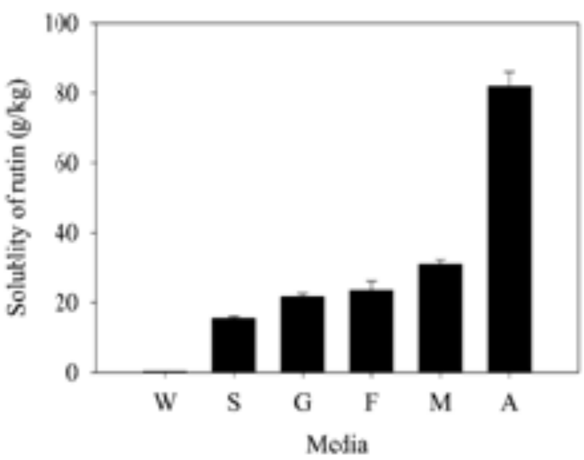


Figure 2. Comparison of rutin solubility (g kg^{-1}) in water (W), S choline chloride (S), Glc-choline chloride (C), Fru-choline chloride (F), malic acid-choline chloride (M), and aconitic acid-choline chloride (A).

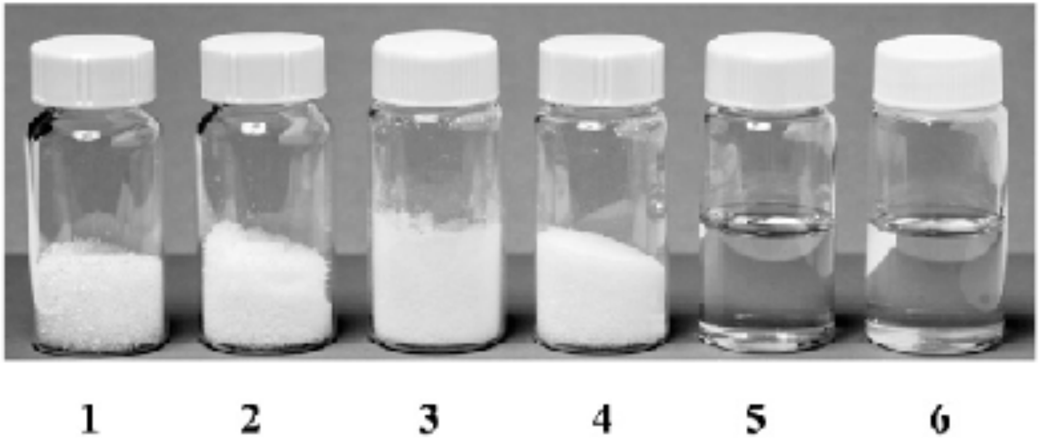
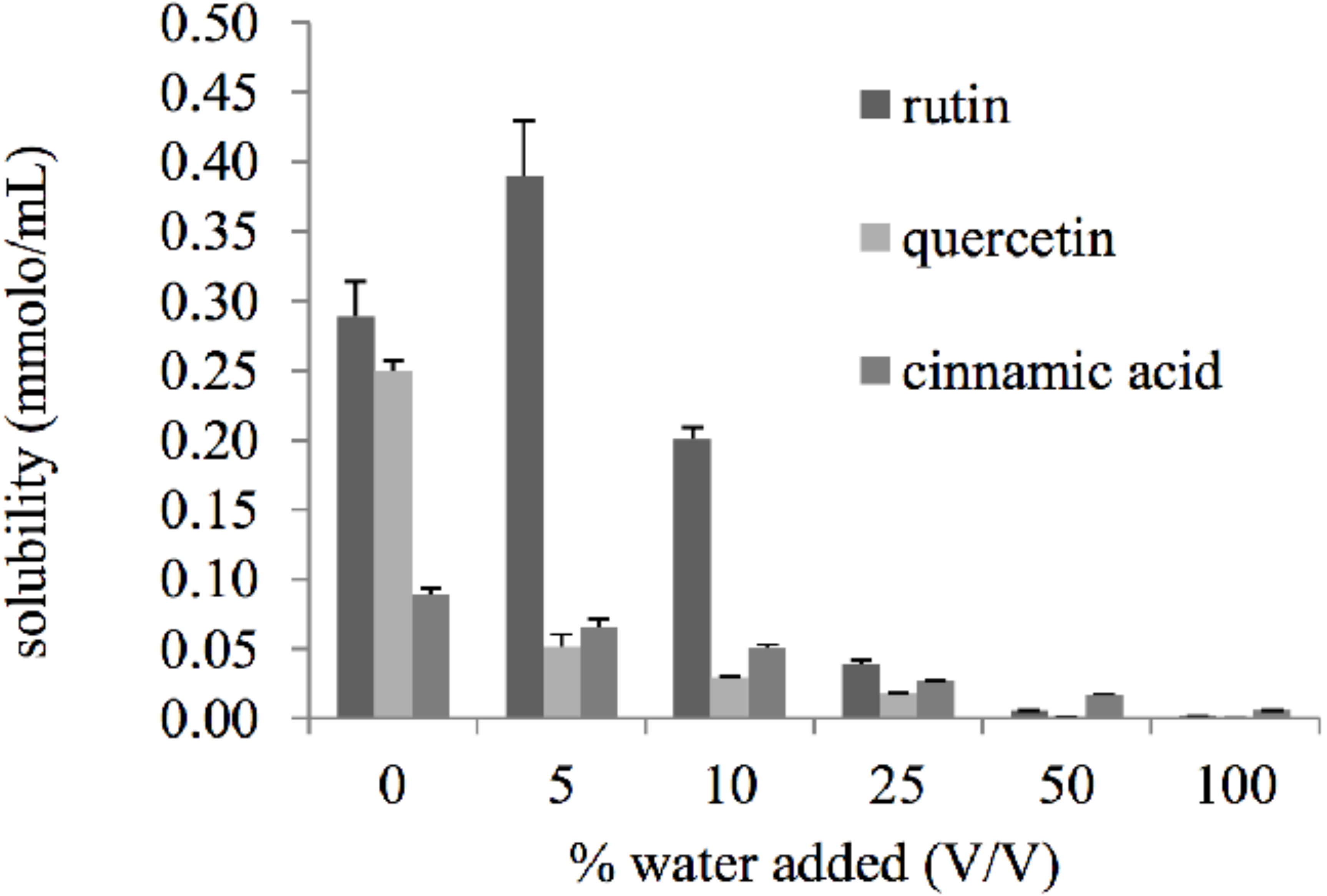
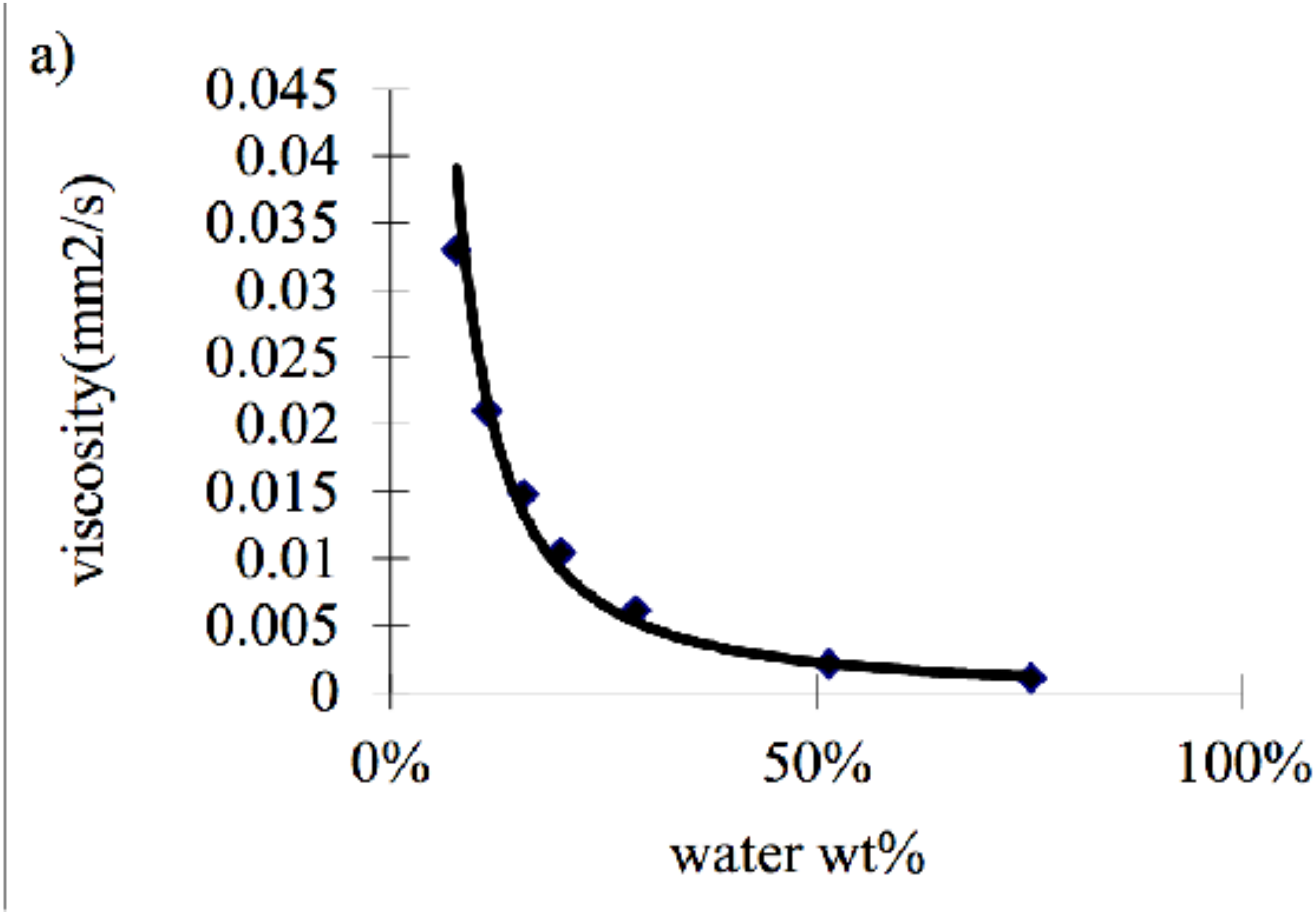


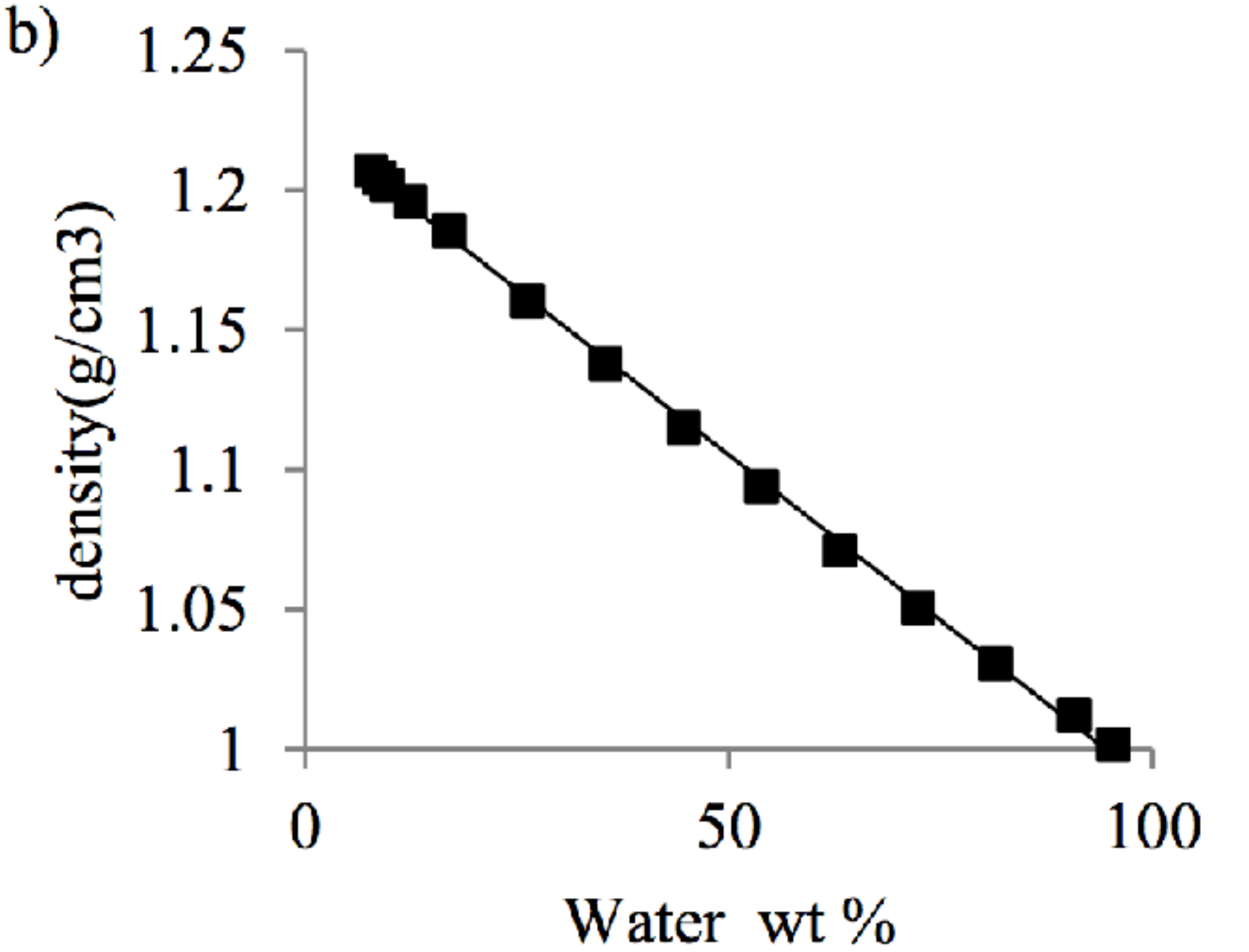
Figure 4. Typical natural eutectic solvents. Container 1, Suc; container 2, Fru; container 3, Glc; container 4, malic acid; container 5, Suc:Fru:Glc (1:1:1, molar ratio); container 6, Suc:malic acid (1:1, molar ratio).



0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
solubility (mmolo/mL)
rutin
quercetin
cinnamic acid
0
5
10
25
50
100
% water added (V/V)

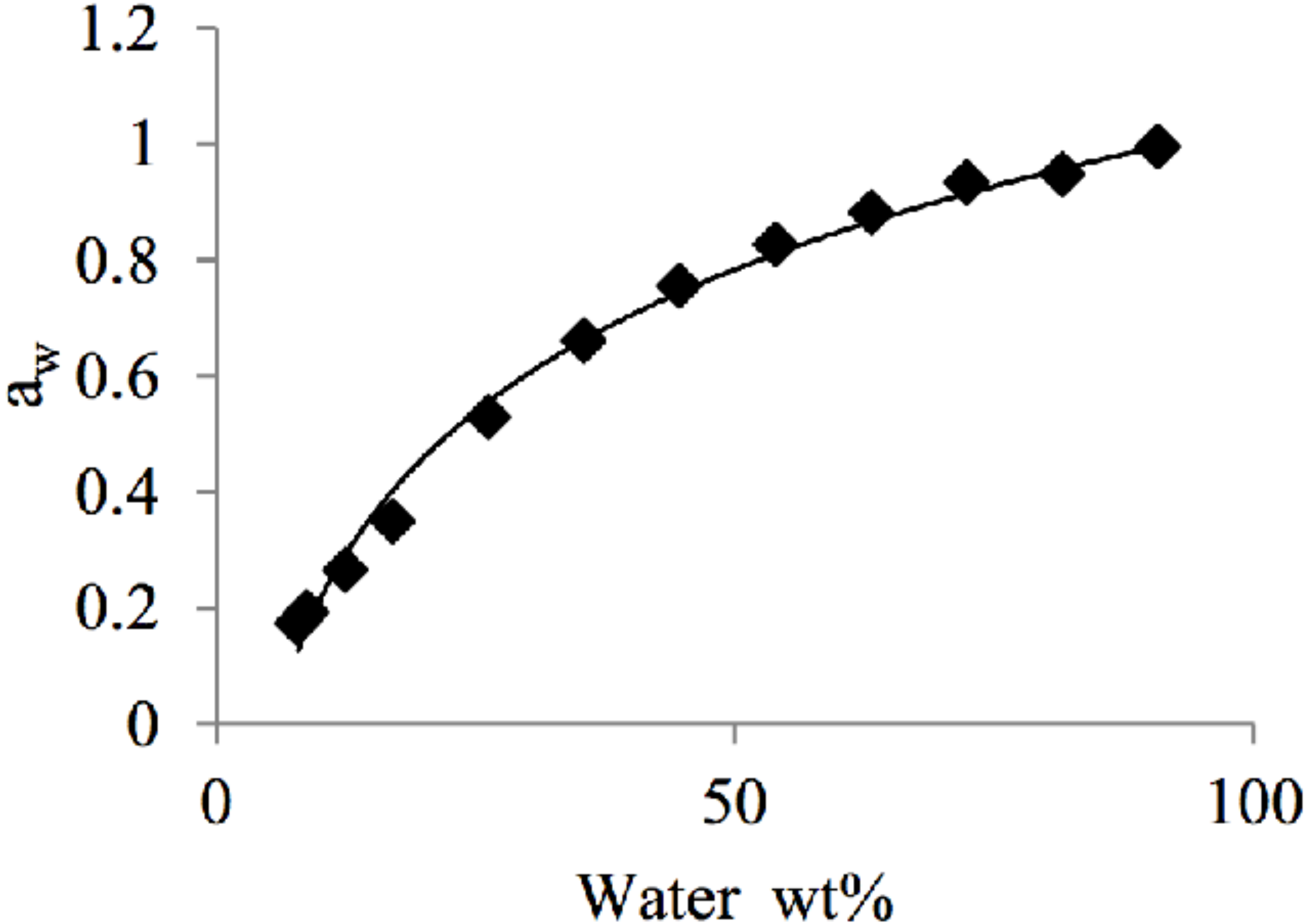
Dai, dissertation. Glucose-choline. (1:2.5).





API)

c)



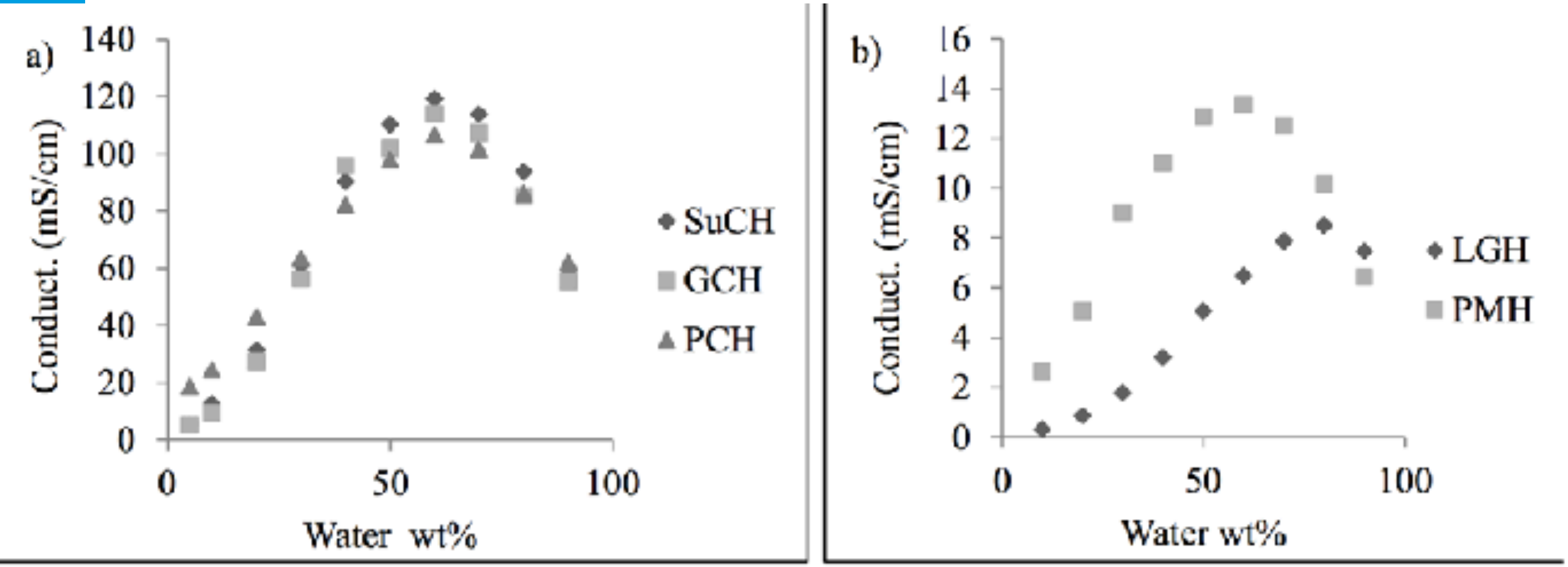
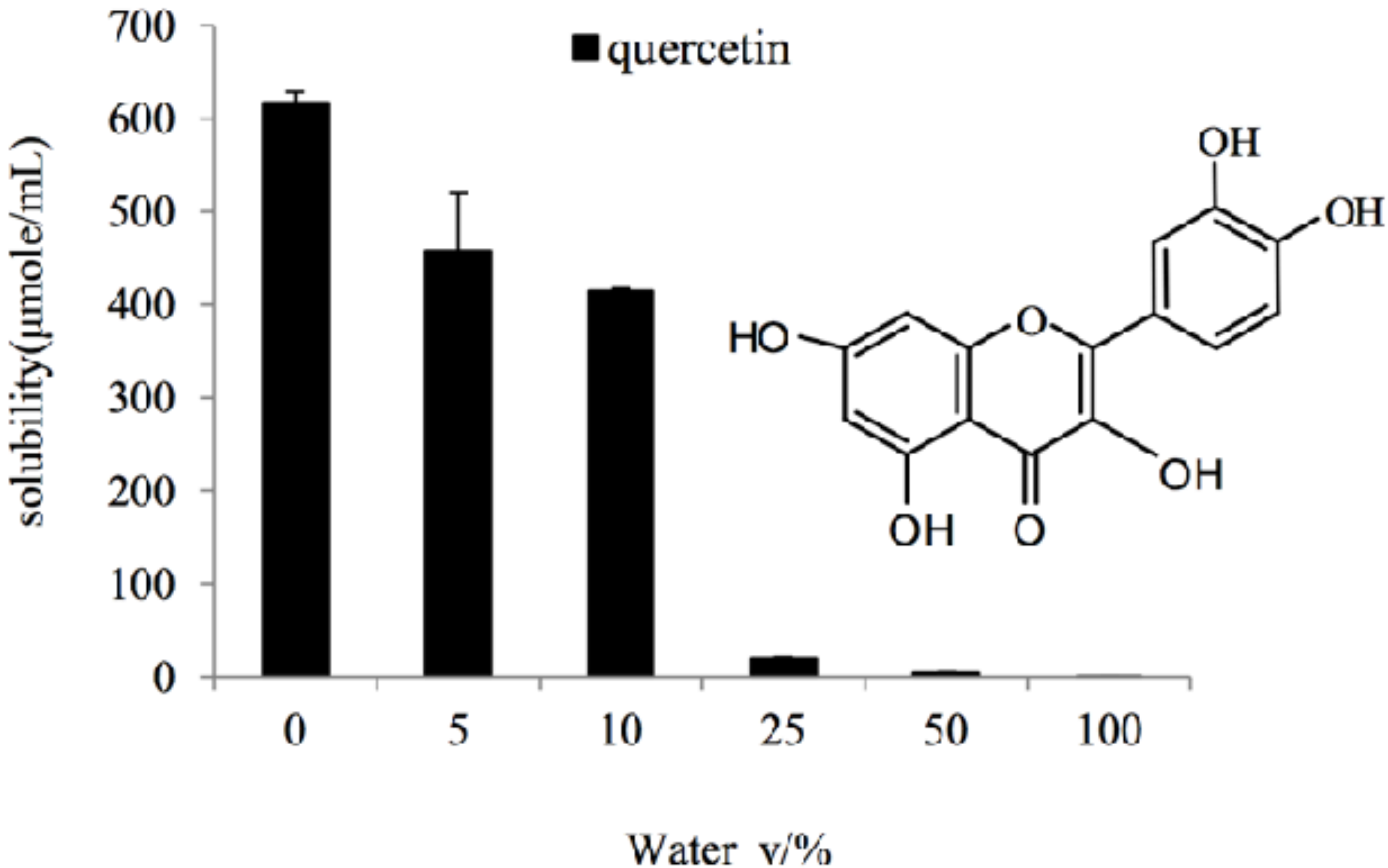


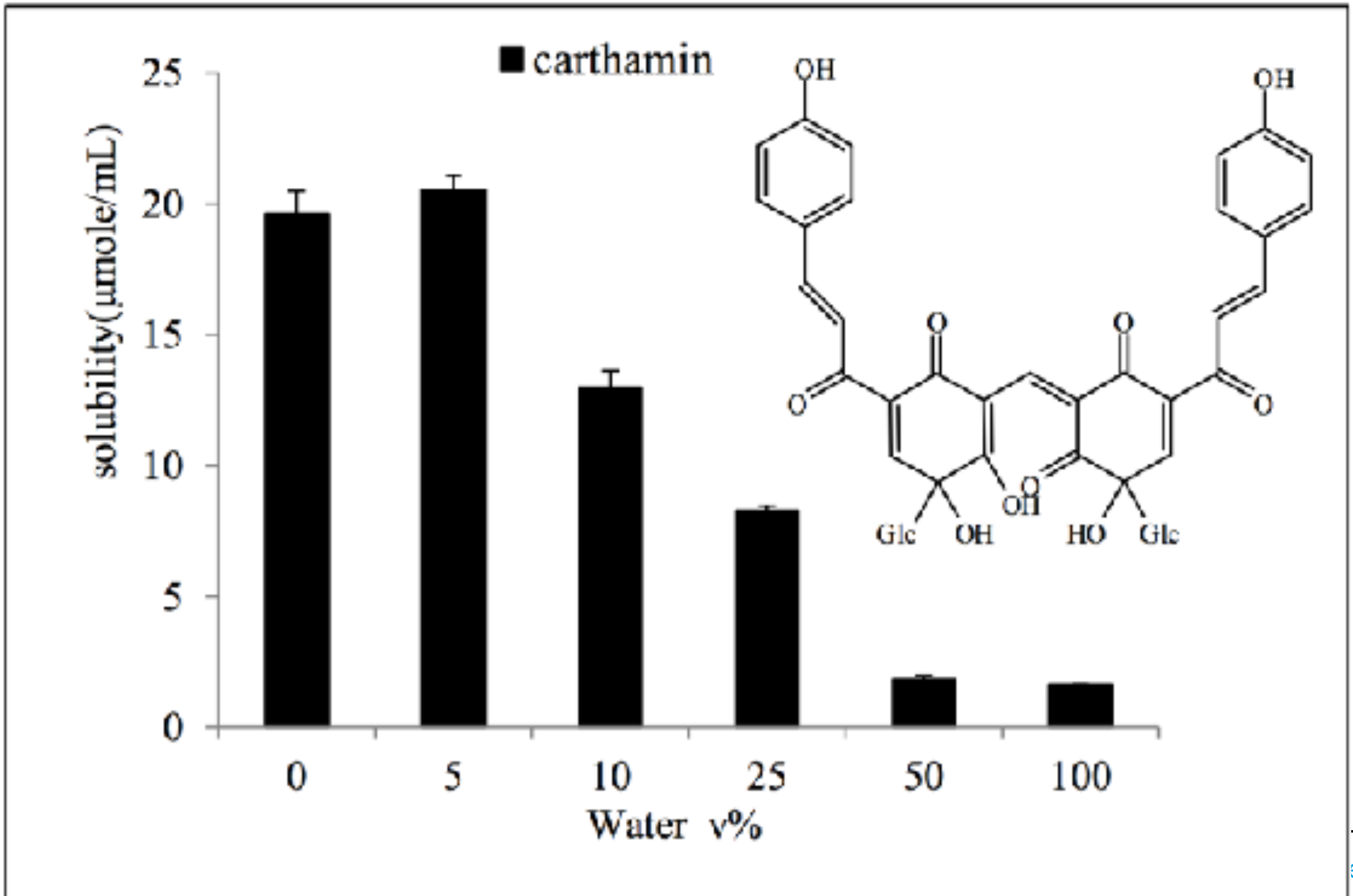
Fig. 6. Conductivity data of diluted NADES at ambient temperature (27 ºC) of **a)** sucrose: choline chloride: water (1:4:4, SuCH), glucose: choline chloride: water (2:5:5, GCH), 1,2-propanediol-choline chloride (1:1:1, PCH), and of **b)** lactic acid-glucose (5:1:3, LGH).

The solubility of quercetin and carthamin in

1,2-propanediol-choline chloride-water (1:1:1, molar ratio)

diluted with a different percentage of water.




carthamin
solubility(µmole/mL)
25
20
15
10
5
0
0
5
10
25
50
100
Water v%
OH
OH
O
O
O
O
O
O
OH
Glc
OH
HO
Glc

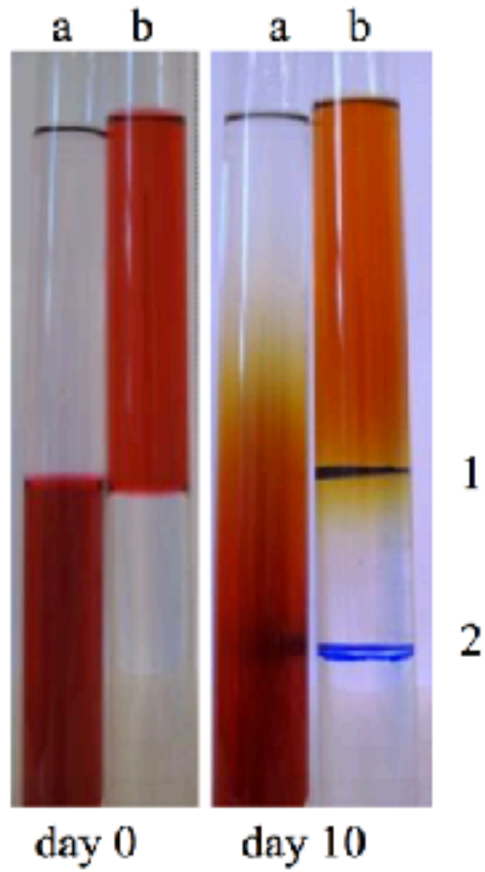


Fig.3 The picture of diffusion tests between sucrose-choline chloride-water (1:4:4) and water on day 0 and 10, and 3 layers were observed with two interfaces (line 1 and 2) labeled in blue on day 10.

*Process Equipment Section (Apparatenbouw Procesindustrie, API)

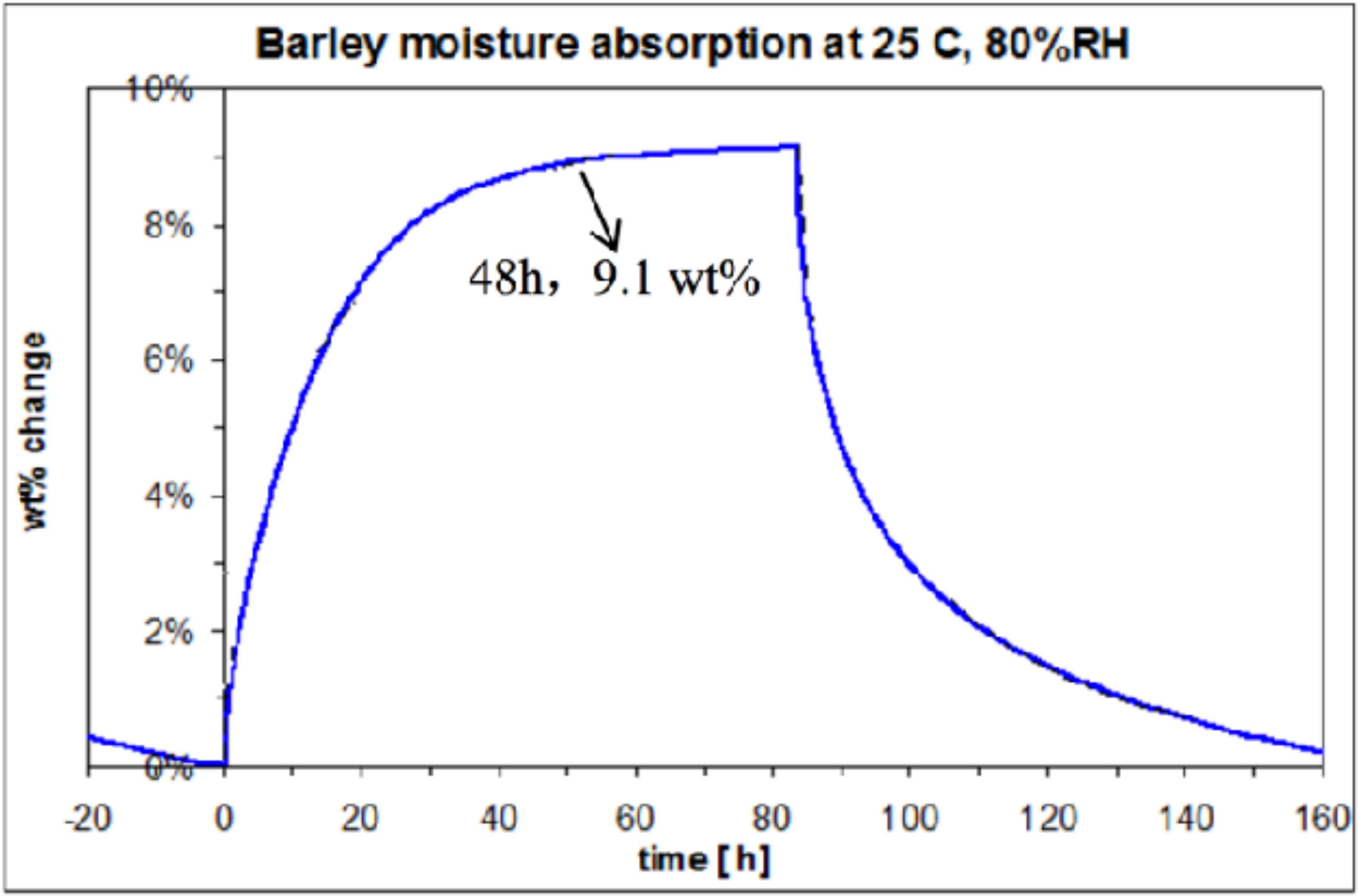
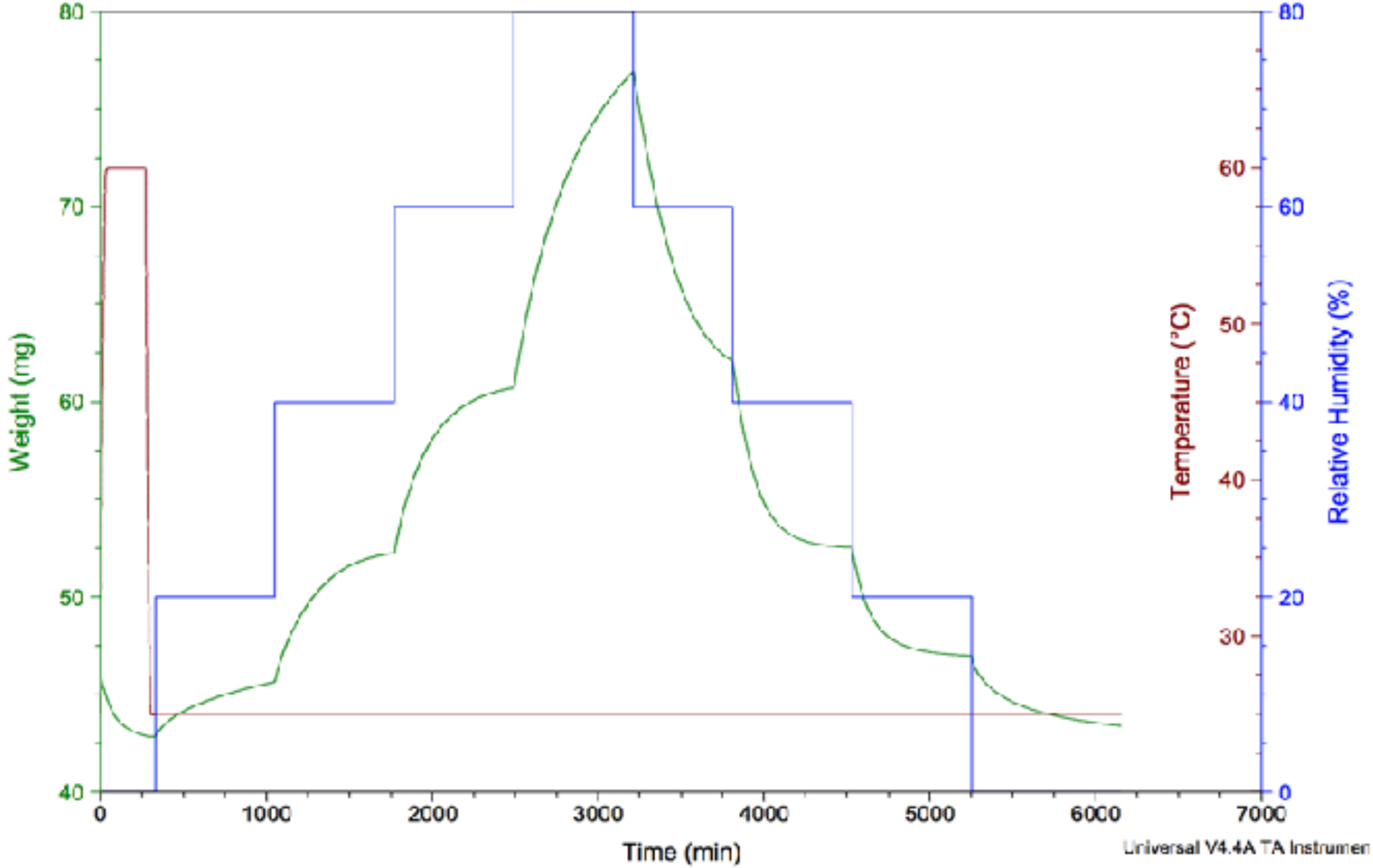


Fig. 5 The hygroscopicity test of barley seeds at 25 °C with 80% relative humidity level.



TUDelft

*Process Equipment Section (Apparatenbouw Procesindustrie, API)

A. Paivo et al, ACS sust. chem. & eng. 2 (2014)1063

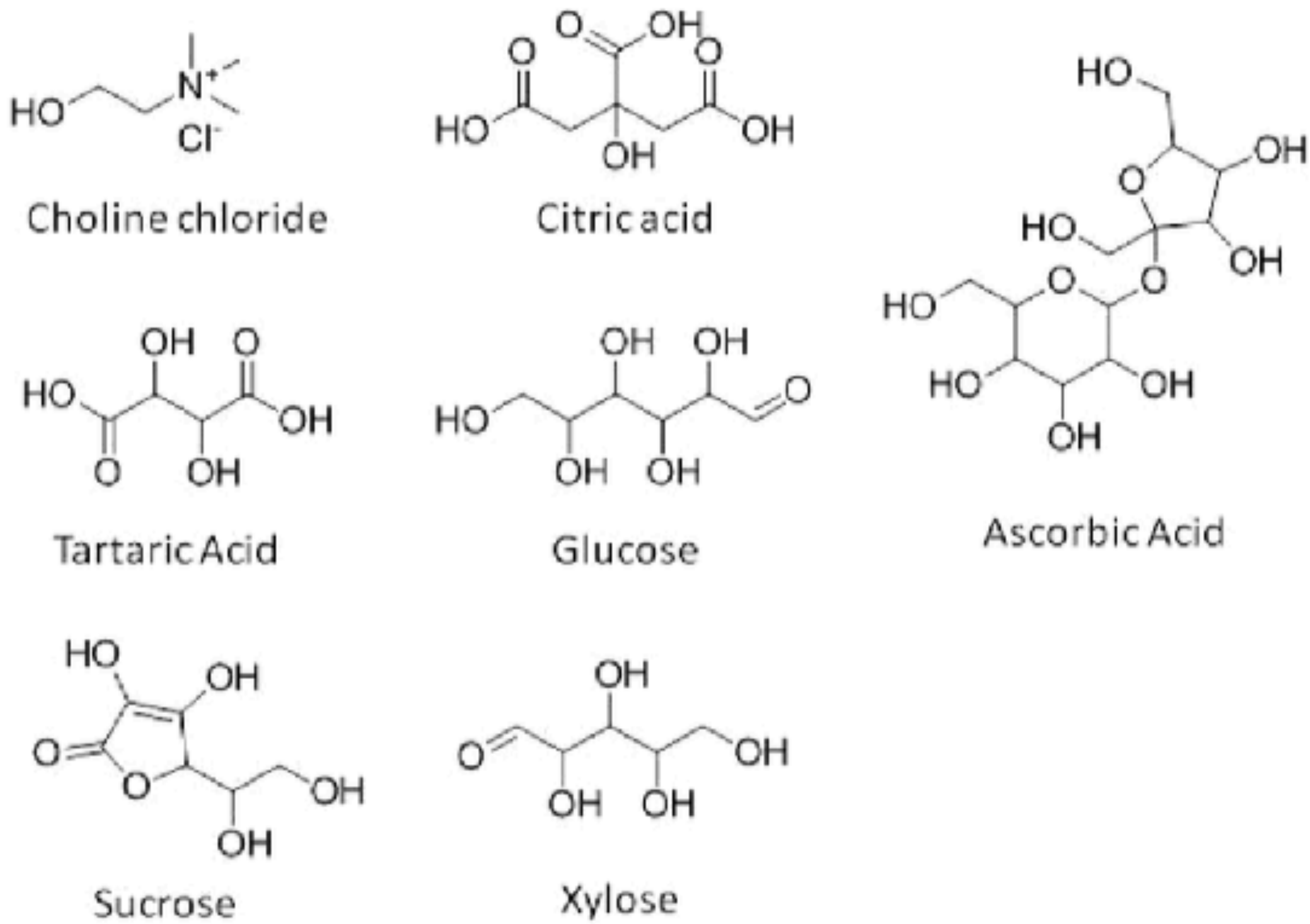


Figure 2. Chemical structure of different compounds with the ability to form natural deep eutectic solvents.

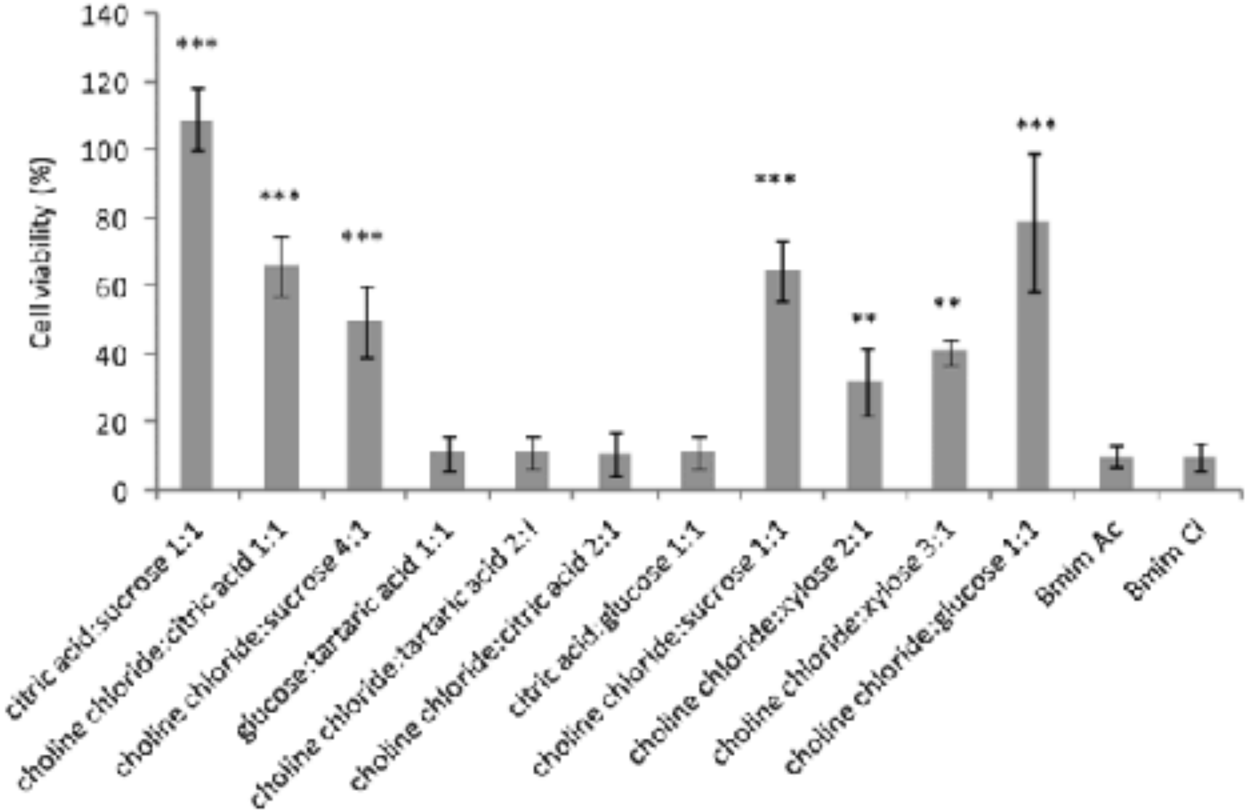
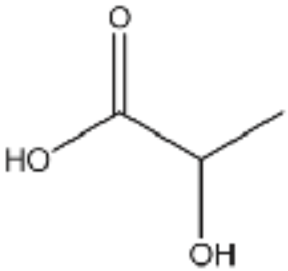
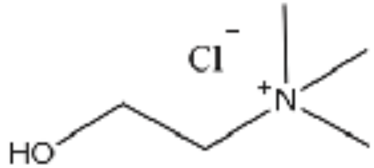


Figure 7. Citotoxicity studies of different NADES in comparison with two ionic liquids. ** denotes statistical significance at $p < 0.01$, and *** denotes $p < 0.001$ level.

Example NADES



Lactic Acid

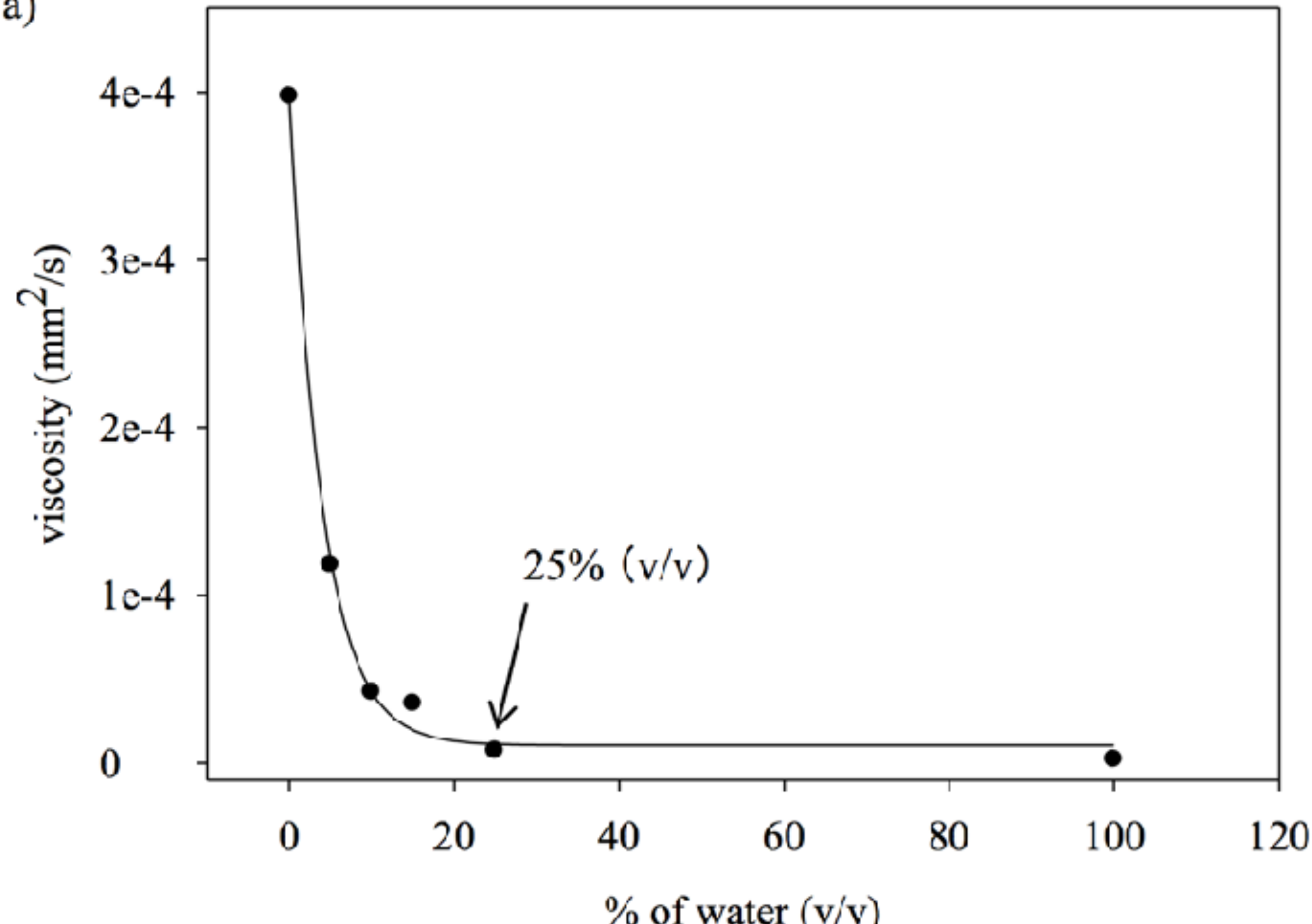


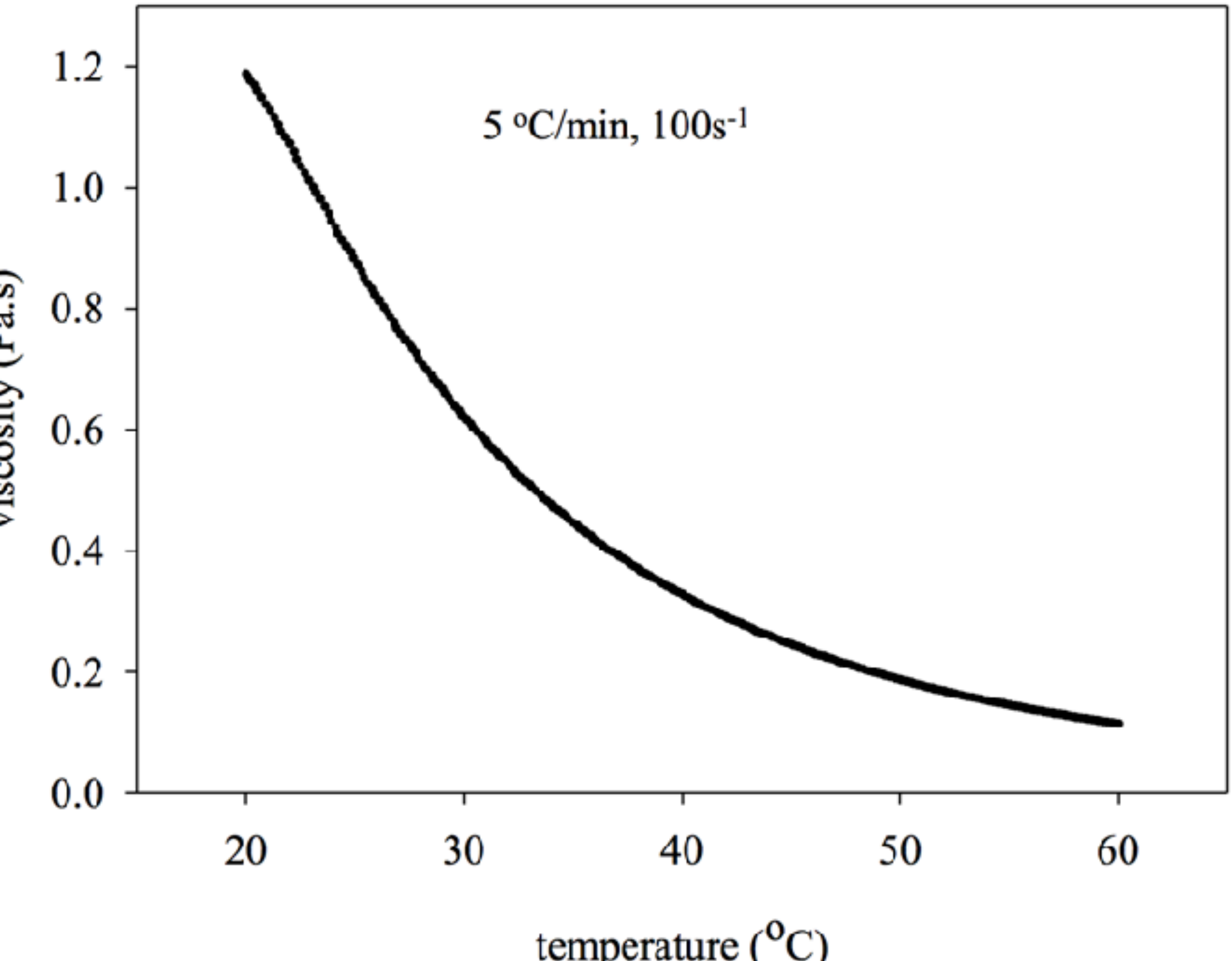
Choline Chloride

Component	Molar mass (g mol^{-1})	Melting point (K)
Lactic acid	90.08	326
Choline chloride	139.62	575[a]
LC 15:1	93.18	206[b]

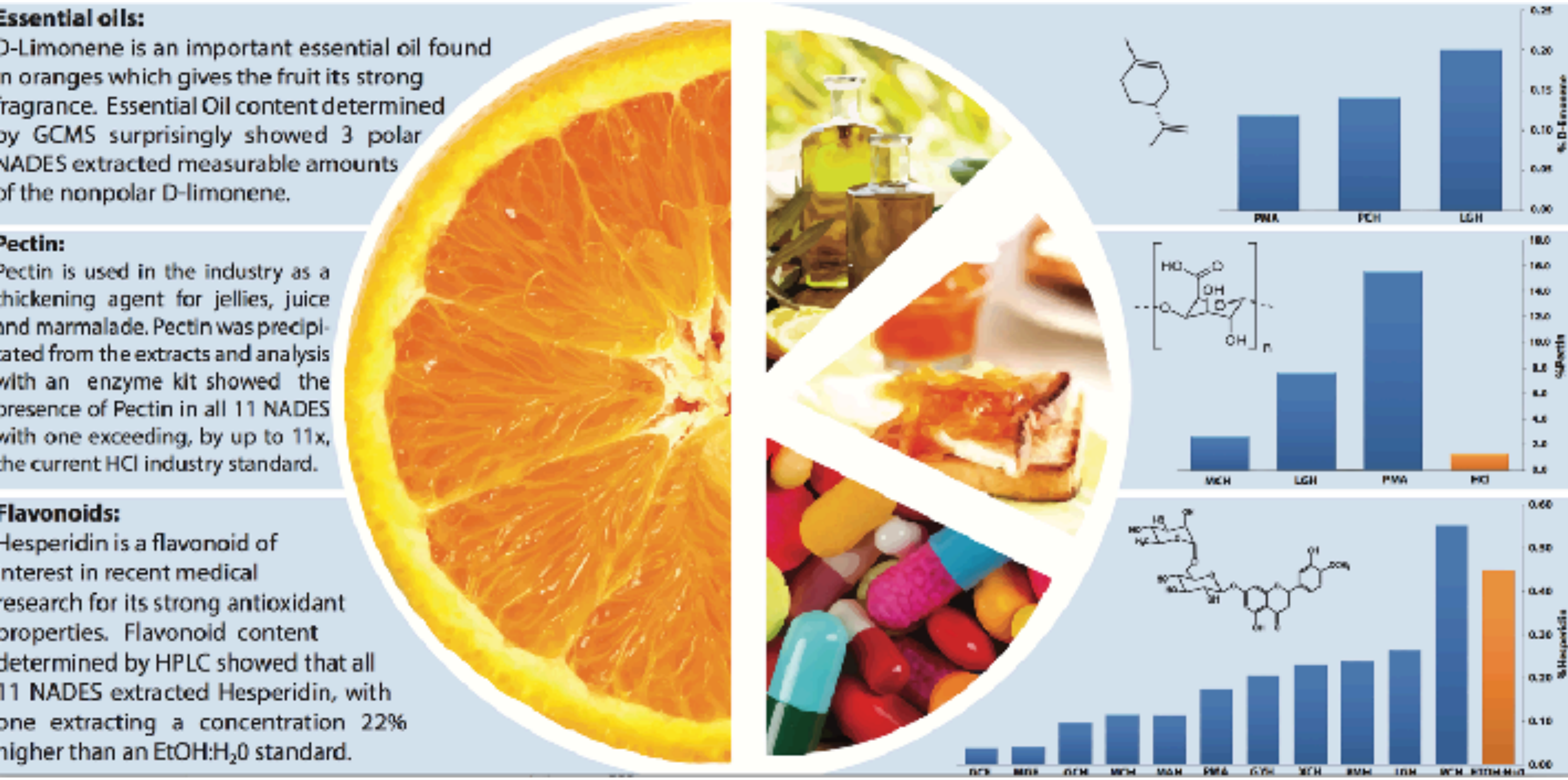
[a] Decomposition temperature.
[b] Glass transition temperature.

M. Francisco et al, FLuid Phase Eq. 340 (2013) 77 a)


viscosity (mm^2/s)
4e-4
3e-4
2e-4
1e-4
0
25% (v/v)
0
20
40
60
80
100
120
% of water (v/v)


5 °C/min, 100s-1
1.2
1.0
0.8
0.6
0.4
0.2
0.0
20
30
40
50
60
temperature (°C)
viscosity (Pa.s)

NADES allow specific separations



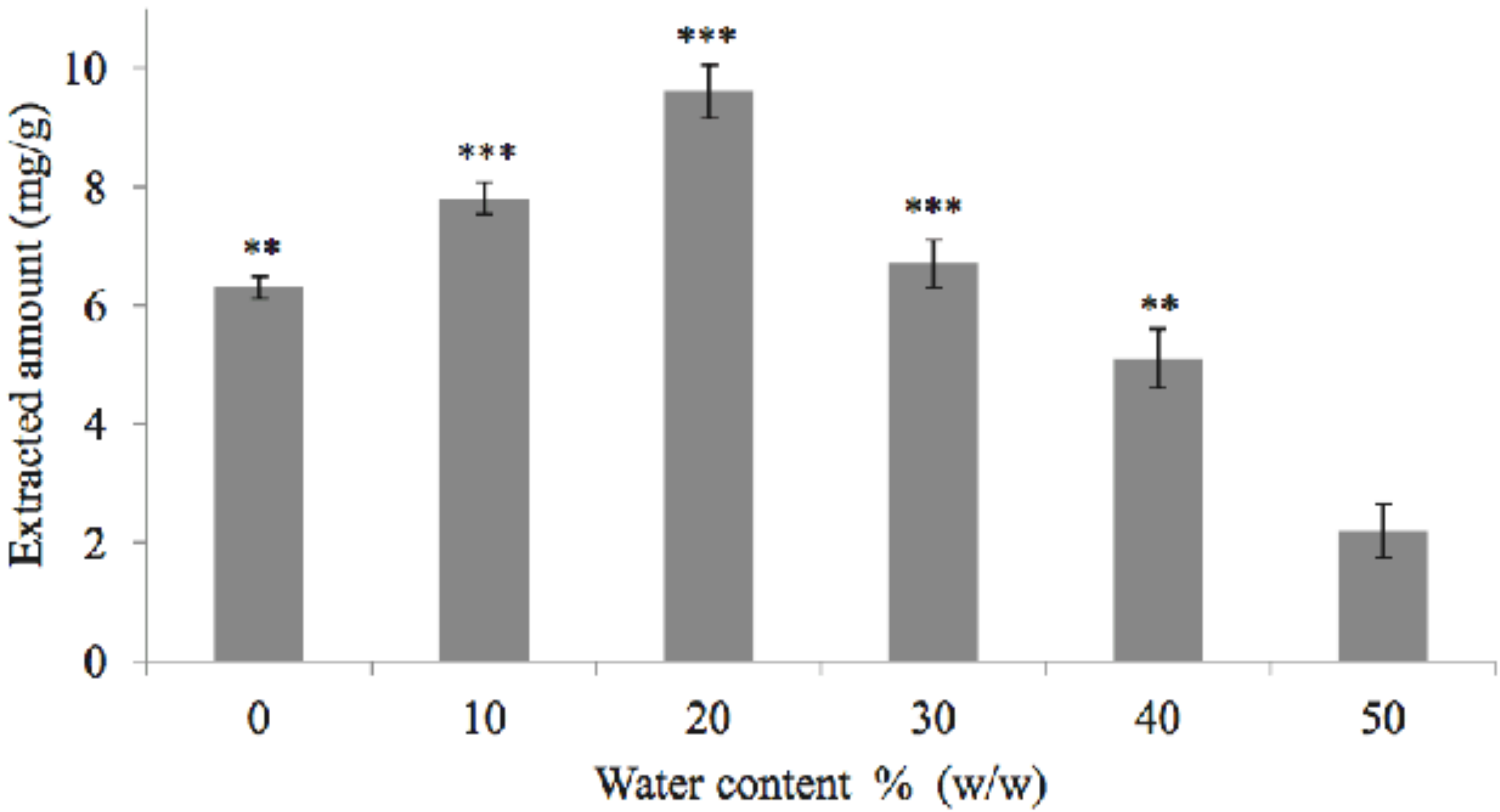


Fig. 2. Effect of ChGly water contenton the extraction efficiency of rutin. Extraction conditions: 40 mg of tartary buckwheat hull powder, 1.0 mL solvent, 40 °C, 1 h, UAE power 200 W. Extraction efficiencies that were significantly higher in comparison with that of 50% ChGly are indicated with $^{*}p < 0.05$, $^{**}p < 0.01$, and $^{***}p < 0.001$.

Process with NADES

- Solubility of rutin in ChGly NADES has a maximum in 20% water.
- A process would extract rutin with ChGly20, recover rutin by precipitation using H2O as antisolvent, ant regenerating the NADES by evaporation of the water (maybe crystallisation).
- For other systems back extraction with water (acidic, basic or neutral) worked out.

solubility of CO2 in a DES (butanediol/ChCl)

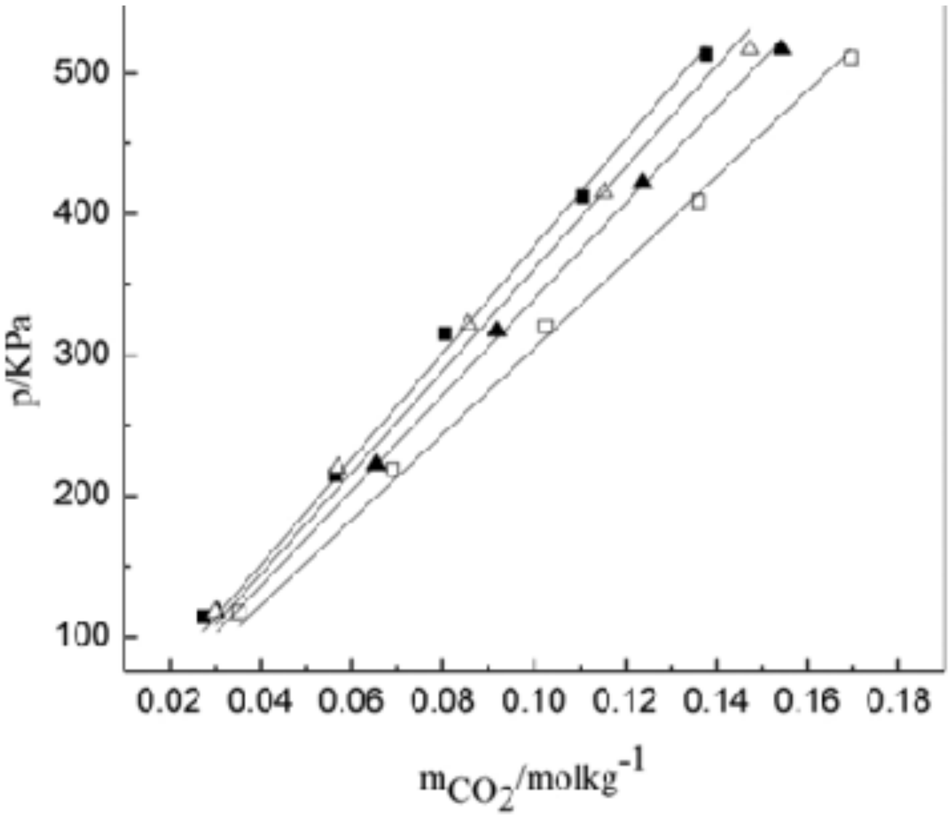


Figure 4. CO_2 solubility, expressed as CO_2 molality (m_{CO_2}), as a function of CO_2 equilibrium pressure (p_{CO_2}) at T = 303.15 K in DESs. ■, n_{CC}:$n_{2,3\text{-butanediol}}$ = 1:3 ; □, n_{CC}:$n_{2,3\text{-butanediol}}$ = 1:4; ▲, n_{CC}:$n_{1,2\text{-propanediol}}$ = 1:3; △, n_{CC}:$n_{1,2\text{-propanediol}}$ = 1:4; —, linear fit.

Natural deep eutectic solvents in combination with ultrasonic energy as a green approach for solubilisation of proteins: application to gluten determination by immunoassay

H. Lores, V. Romero, I. Costas, C. Bendicho, I. Lavilla*

Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

Evaluation of new natural deep eutectic solvents for the extraction of isoflavones from soy products

Sylwia Bajkacz[a,*], Jakub Adamek[b]

[a] *Department of Inorganic, Analytical Chemistry and Electrochemistry, Faculty of Chemistry, Silesian University of Technology, M. Strzody 7, 44-100 Gliwice, Poland*
[b] *Department of Organic and Bioorganic Chemistry and Biotechnology, Faculty of Chemistry, Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland*

Production of Poly(vinyl alcohol) (PVA) Fibers with Encapsulated Natural Deep Eutectic Solvent (NADES) Using Electrospinning

Francisca Mano,[†] Ivo M. Aroso,[†,§] Susana Barreiros,[†] João Paulo Borges,[‖] Rui L. Reis,[†,§] Ana Rita C. Duarte,[‡,§] and Alexandre Paiva*[,†]

[†]LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[‡]3B's Research Group—Biomaterials, Biodegradable and Biomimetic, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, Avepark, 4805-017 Taipas, Guimarães, Portugal

[§]ICVS/3B's PT Government Associate Laboratory, 4710-057 Braga/Guimarães, Portugal

[‖]CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

Thermal and physical properties of (Choline chloride + urea + L-arginine) deep eutectic solvents

Fareeda Chemat [a], Hirra Anjum [a], Azmi Md Shariff [a], Perumal Kumar [b], Thanabalan Murugesan [a,*]

[a] *Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia*
[b] *Department of Chemical Engineering, Curtin University, Miri, 98009, Sarawak, Malaysia*

NADES

- Some stabilise natural polymers including proteins against drought, high or very low temperatures, oxidation, microbes.
- At low water content they are hygroscopic.
- Visocity decreases markedly with increasing water content.

Conclusions

Even though many aspects of NADES are not understood yet, these food grade solvents already are very useful in food technology.

Eutectic systems can contribute in various ways to food grade green chemistry

Processes based on cooling or high pressures can be very attractive

FOOD stars Innovative Food Product Development Cycle: Frame for Stepping Up Research Excellence of FINS

Some properties of and processes with Green Solvents

Workshop Novi Sad 27-29 May 2017

Geert-Jan Witkamp, Delft University of Technology

Conclusion

- Even though many aspects of NADES are not understood yet, these food grade solvents already are very useful in food technology.
- Eutectic systems can contribute in various ways to food grade green chemistry
- Processes based on cooling or high pressures can be very attractive

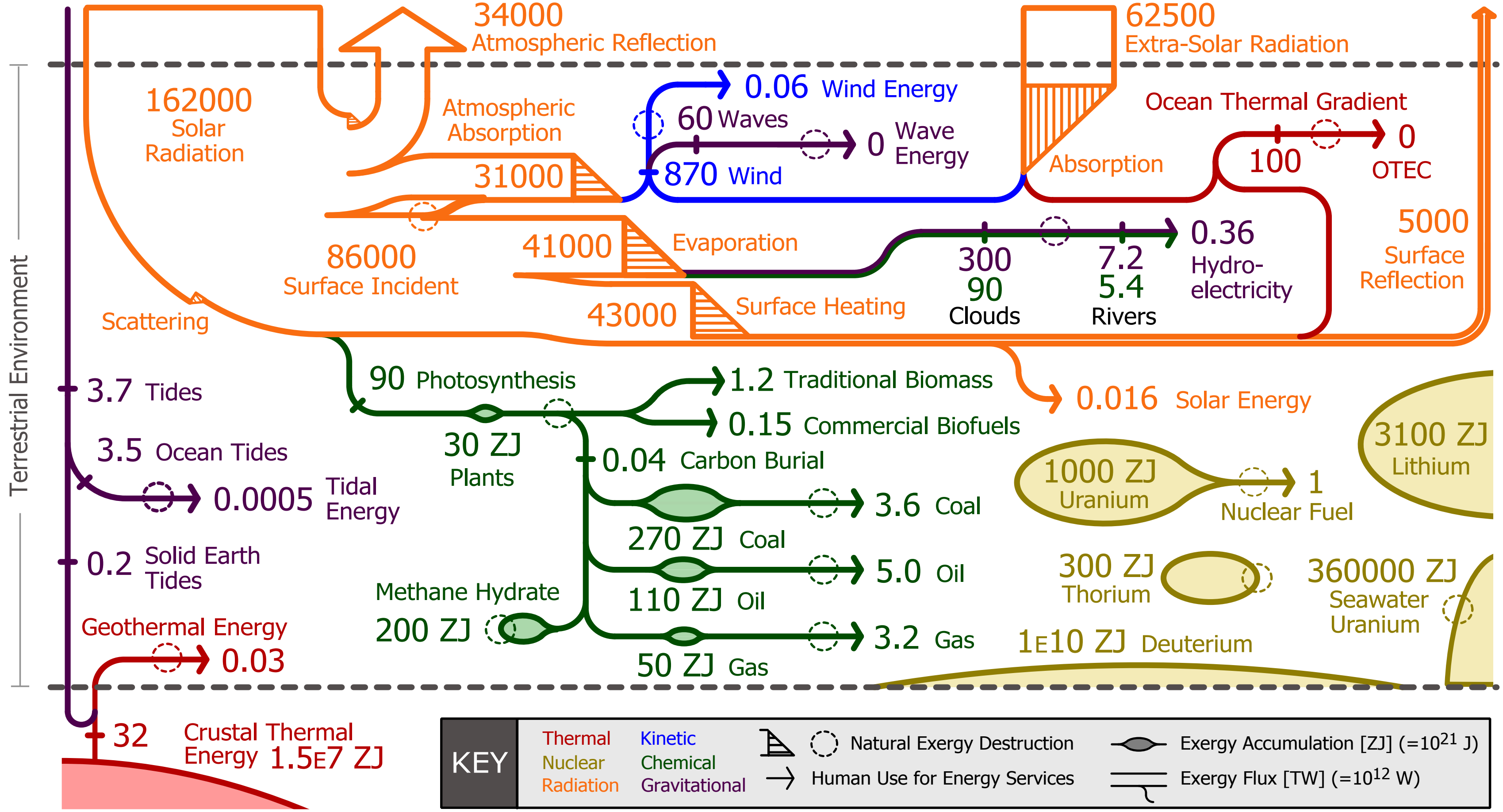
New biorelated topics

- role of the hydrogen bridge in NADES, physical explanation (liquid crystal, bond exchange rate)
- recovery of biopolymers from water treatment
- profiling and role of (ultra)trace elements (w Peter Leon, Gijs)
- eutectic freeze crystallisation for DSP, eg of FDCA (with BPF)
- extraction and concentration of natural products using NADES (combi scCO2) (w Leiden)
- crystallisation fouling on membranes (w Hans Vrouwnv)

Other topics (wetsus)

- Closed loop ion exchange regenerate recovery (drinking water)
- Closed loop antiscalant recovery
- Ice growth on cooled surfaces
- Robust modular software for Pitzer based prediction of water and ion activity in aqueous solutions
- Solar desalination
- Light driven separations

Global Exergy Flux, Reservoirs, and Destruction



Exergy is the useful portion of energy that allows us to do work and perform energy services. We gather exergy from energy-carrying substances in the natural world we call energy resources. While energy is conserved, the exergetic portion can be destroyed when it undergoes an energy conversion. This diagram summarizes the exergy reservoirs and flows in our sphere of influence including their interconnections, conversions, and eventual natural or anthropogenic destruction. Because the choice of energy resource and the method of resource utilization have environmental consequences, knowing the full range of energy options available to our growing world population and economy may assist in efforts to decouple energy use from environmental damage.

Prepared by Wes Hermann and A.J. Simon
Global Climate and Energy Project at Stanford University (http://gcep.stanford.edu)

Research

- Crystallisation (precipitation, eutectic freezing)
- Green Solvents (carbon dioxide, natural deep eutectic solvents or NADES)

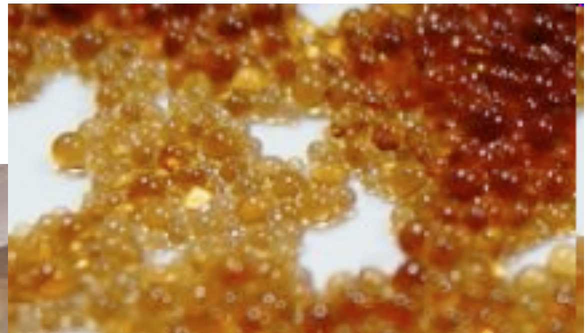
Applied to

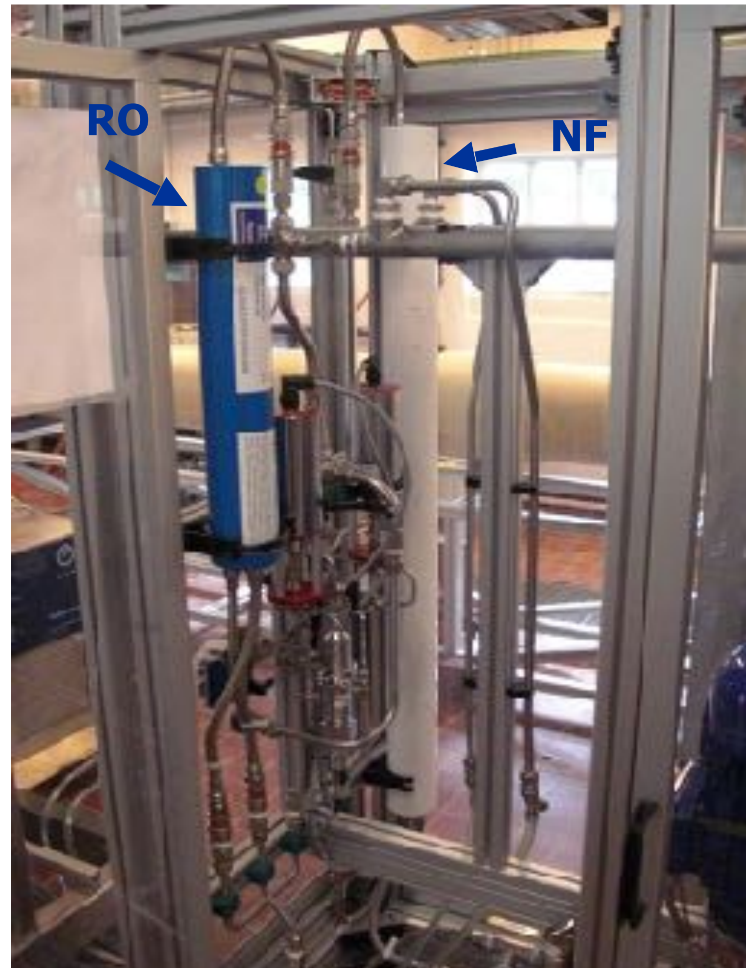
downstream processing, water treatment, drug formulation, natural products recovery, biomineralisation

Questions e.g.

- mechanisms of scaling (surface crystallisation)
- understanding role of NADES in biology
- role of (ultra-) trace elements
- coupled driving forces in cell transport

KWR PILOT PLANT
Ionenwisseling, Nanofiltratie, Rev. Osm.





Berekening **Kosten**

Nu 6.000.000 – 8.000.000 m³ brijn per jaar in Zuid-Holland

↓

Door Hogere Recovery: 2.000.000 – 3.000.000 m³ / jaar

↓

Stel kostprijs verlaging EFC naar € 8,00 / m³ (all–in)

↓

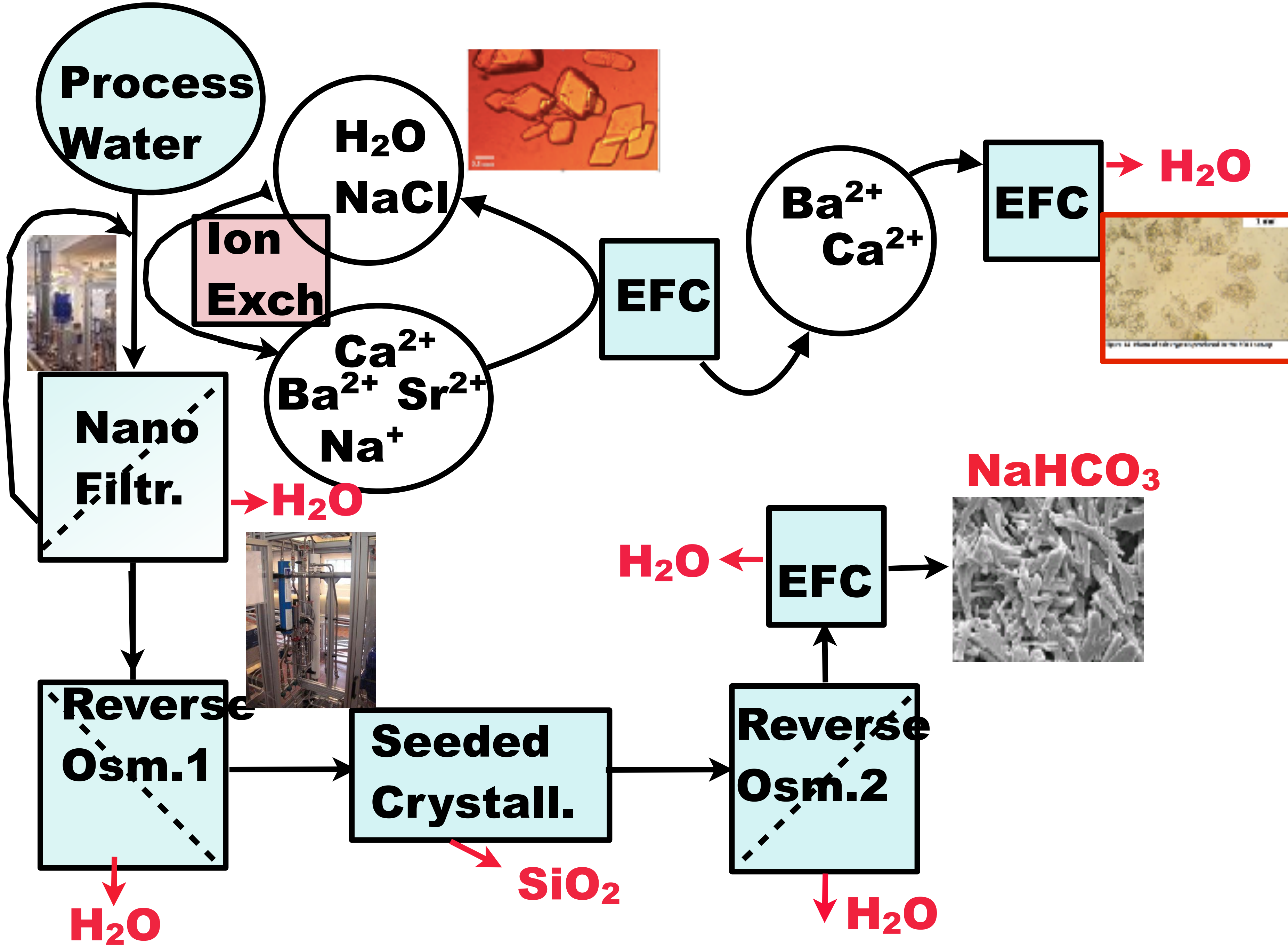
Kosten in Zuid-Holland € 16.000.000,- á 24.000.000,-

Circa 500 tuinders met brijninfiltratie

↓

Gemiddeld per tuinder € 32.000,- á € 48.000,- / jaar

EFC kan in de toekomst in combinatie met andere technieken een alternatief zijn voor brijn infiltratie

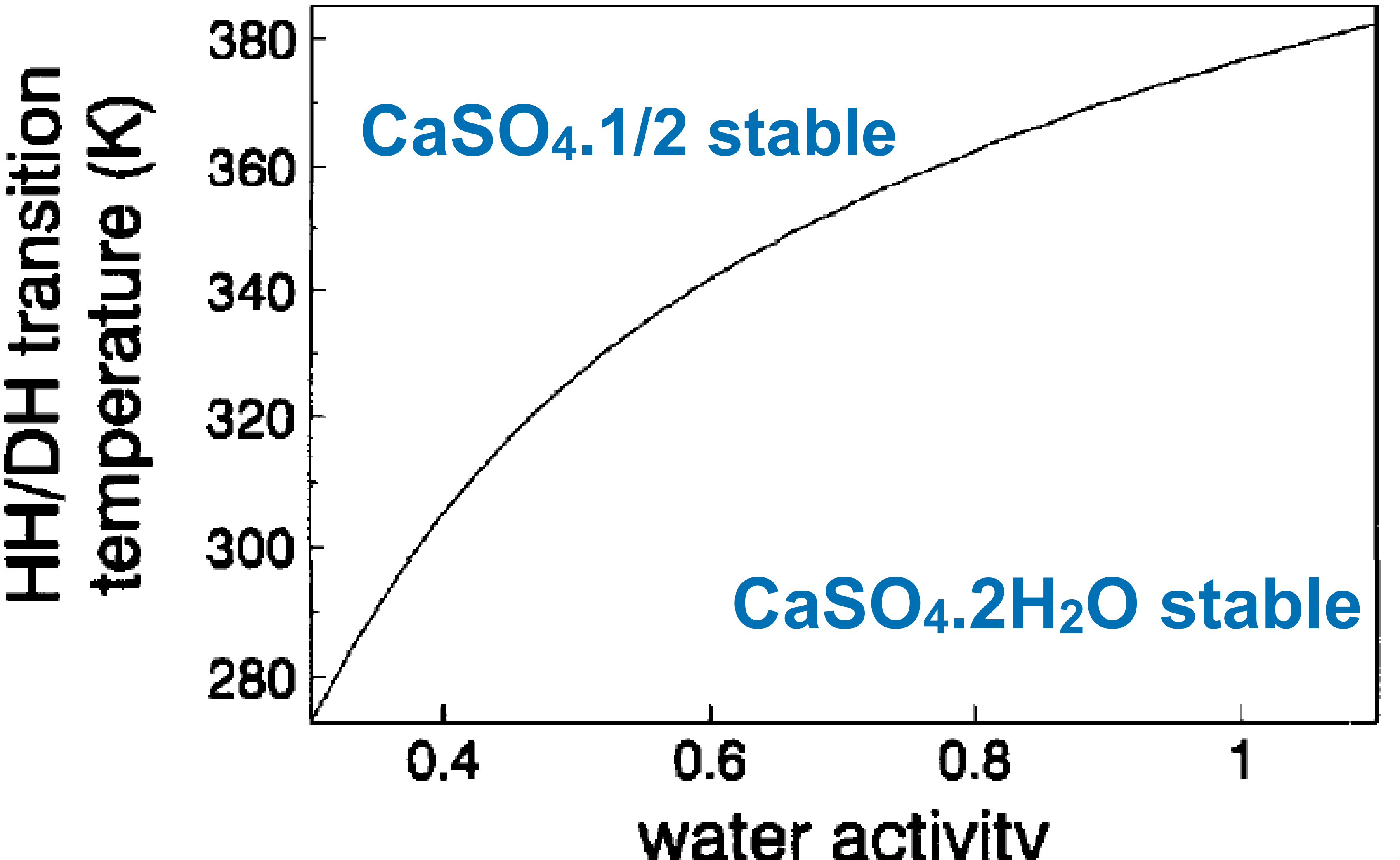


Process Water
H2O NaCl
Ion Exch
Ca2+ Ba2+ Sr2+ Na+
EFC
Ba2+ Ca2+
EFC
H2O
Nano Filtr.
H2O
NaHCO3
H2O
EFC
Reverse Osm.1
Seeded Crystall.
Reverse Osm.2
H2O
SiO2
H2O

Zero Liquid Discharge Water Treatment (reference slide)

- Pretreatment
- UF/RO
- Removal of scalants by Ion Exchange, Liquid Liquid Extraction, Liquid Membrane Extraction etc.
- Removal of scalants in between RO stages by desupersaturation of scaling compounds with in-line crystalliser ($BaSO_4$, $CaCO_3$, SiO_2, $CaSO_4xH_2O$ etc)
- High Recovery RO
- Membrane Distillation
- Membrane Crystallisation
- EFC with in-line removal of scalants by crystalliser, winning of valuable trace elements
- EFC to treat IX regenerates

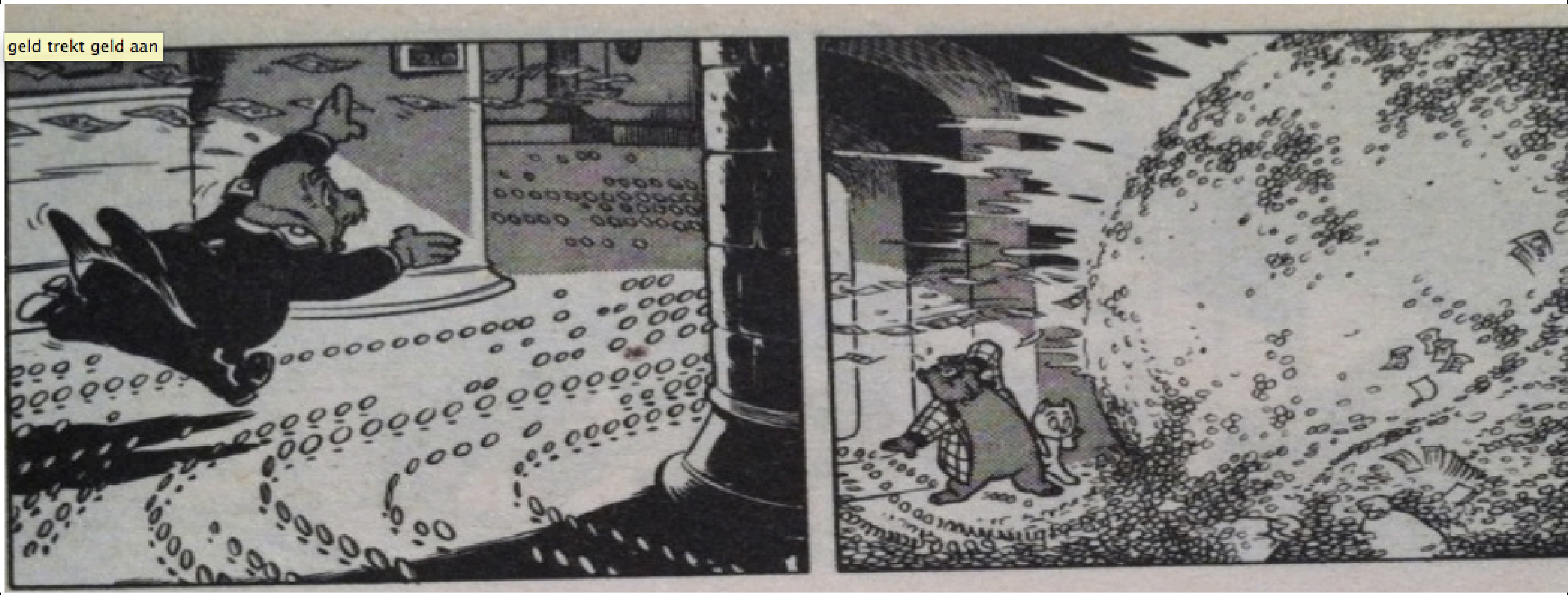
Water activity controls hydrated crystal phase transition temperature



Current crystallisation topics [reference slide]

- Eutectic Freeze Crystallisation: scaling, nucleation, growth, recrystallisation, coupled heat&mass transfer (Onsager), gas hydrates, hydrodynamic design, cooling technology, mechanical design, impurities, fractionation
- Crystallisation from scCO2, ionic liquids,
- Calcium carbonate (scaling, for paper, antiscalants, ultrasound)
- Scaling sensor, scalant removal (Wetsus)
- Silica (anti-)scaling (Wetsus/KWR)
- Electrochemical precipitation (phosphate, iron oxides, carbonate) (Wetsus)
- Scale removal by hydrodynamic cavitation/high intensity waves
- Zero liquid discharge water treatment

Ostwaldripening



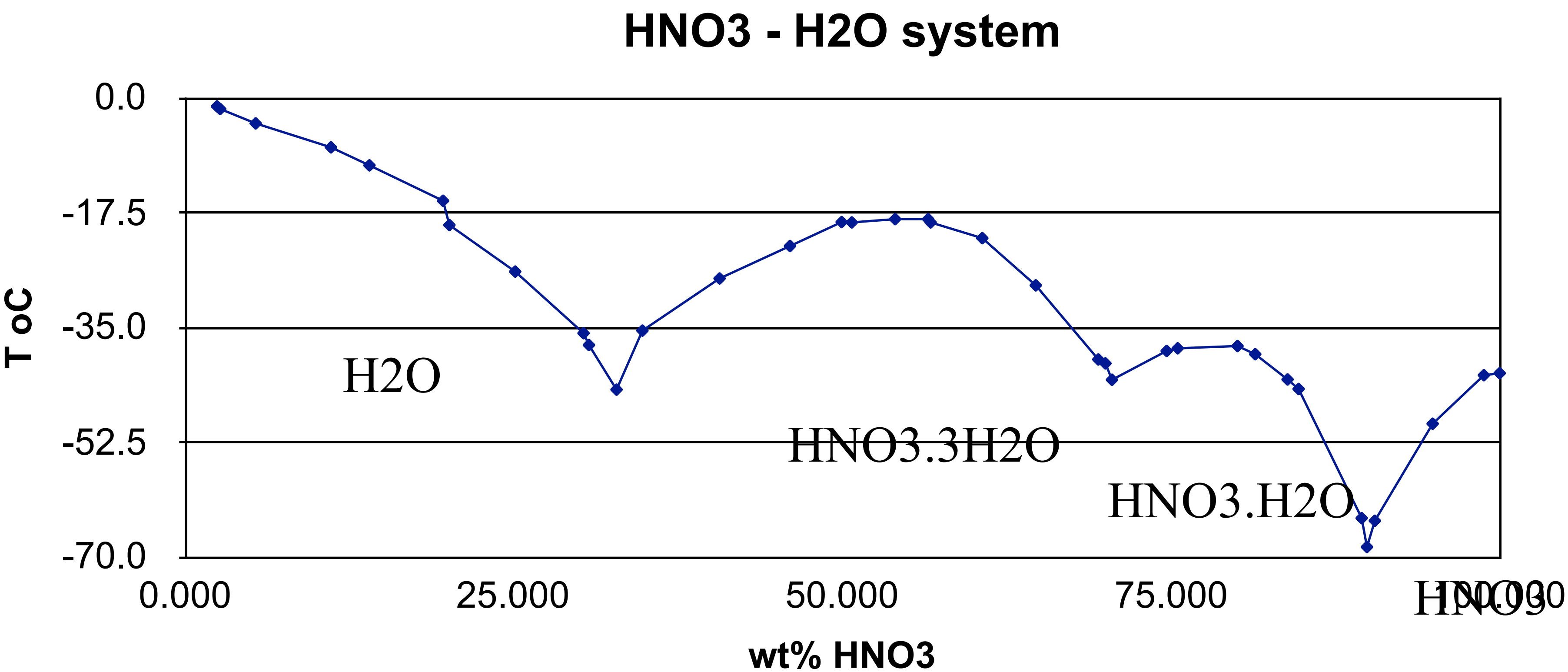
Insert logo university

Green textile dyeing

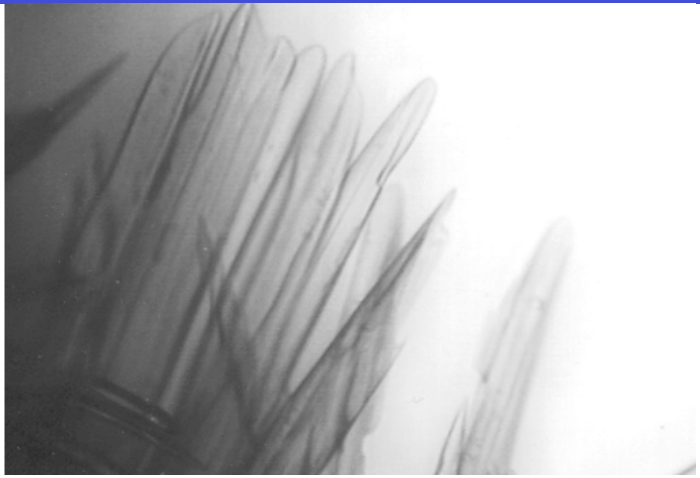
- NADES (natural deep eutectic solvents) for handling natural dyestuffs, enabling currently insoluble compounds to be used
- Carbon dioxide as modifier (co- or antisolvent), lowering viscosity
- In collaboration with Natural Products Laboratory Leiden

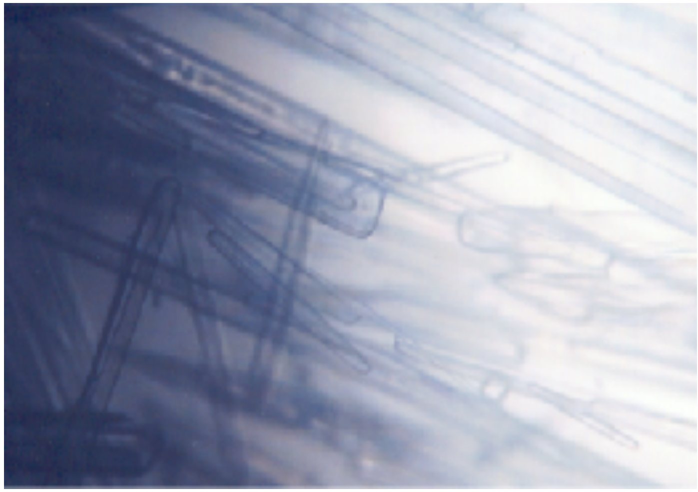
TU Delft

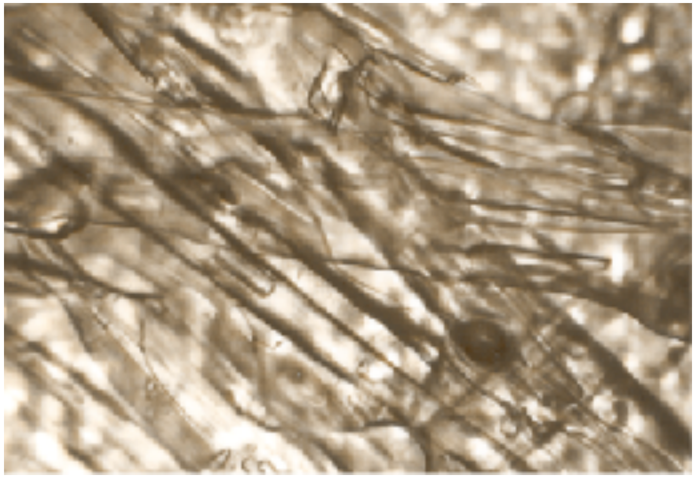
HNO3=H2O phases



$HNO_3.3H_2O$ (Drummond)



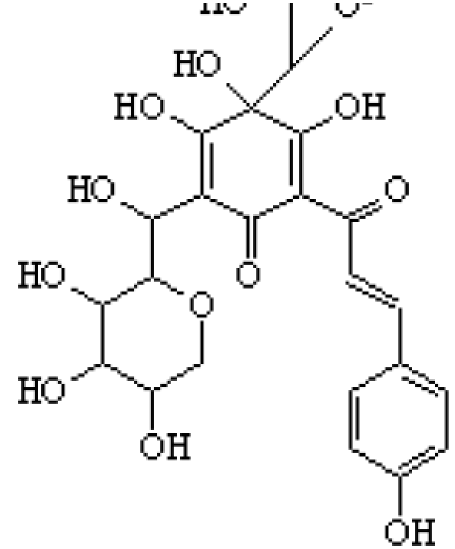




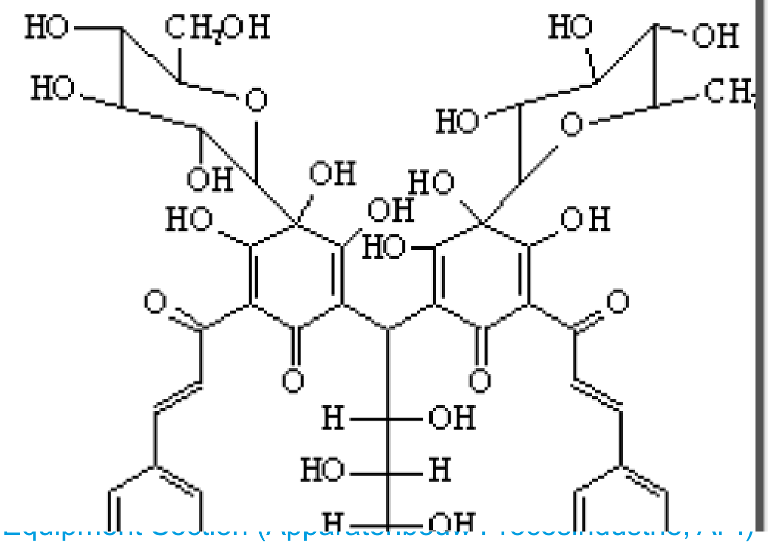
[End Movie]

Safflower (*Carthamus tinctorius* L.)
Formerly as a red dyestuff for textiles; and currently as a minor colourant by the food industry.

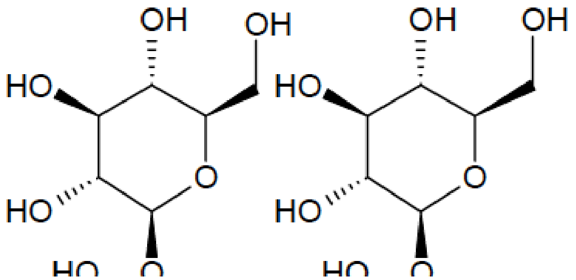
The florets contain three major pigments, all of which are present as chalcone glucosides: the water-insoluble scarlet-red **carthamin** and the water-soluble **"safflor yellow" A and B or safflomin(e) A and B**.



safflomin(e) A (upper) and B (lower)



The term "red tape" originates from the use of safflower to impart a pink-red colour to the tape employed to bind legal documents.



Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Natural deep eutectic solvents as new potential media for green technology

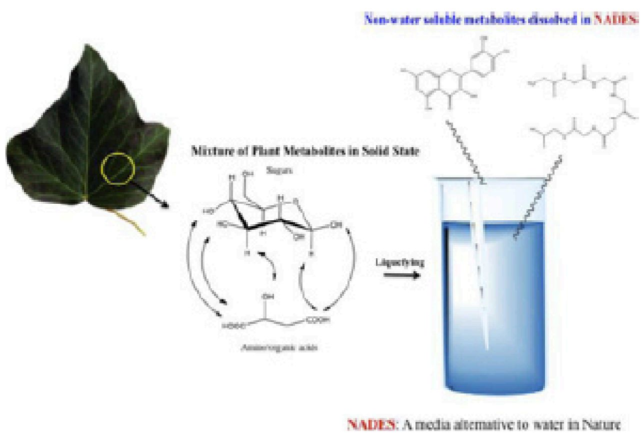
Yuntao Dai [a], Jaap van Spronsen [b], Geert-Jan Witkamp [b], Robert Verpoorte [a], Young Hae Choi [a,*]

[a] Natural Products Laboratory, Institute of Biology, Leiden University, 2300 RA Leiden, The Netherlands
[b] Laboratory for Process Equipment, Delft University of Technology, Delft, The Netherlands

HIGHLIGHTS

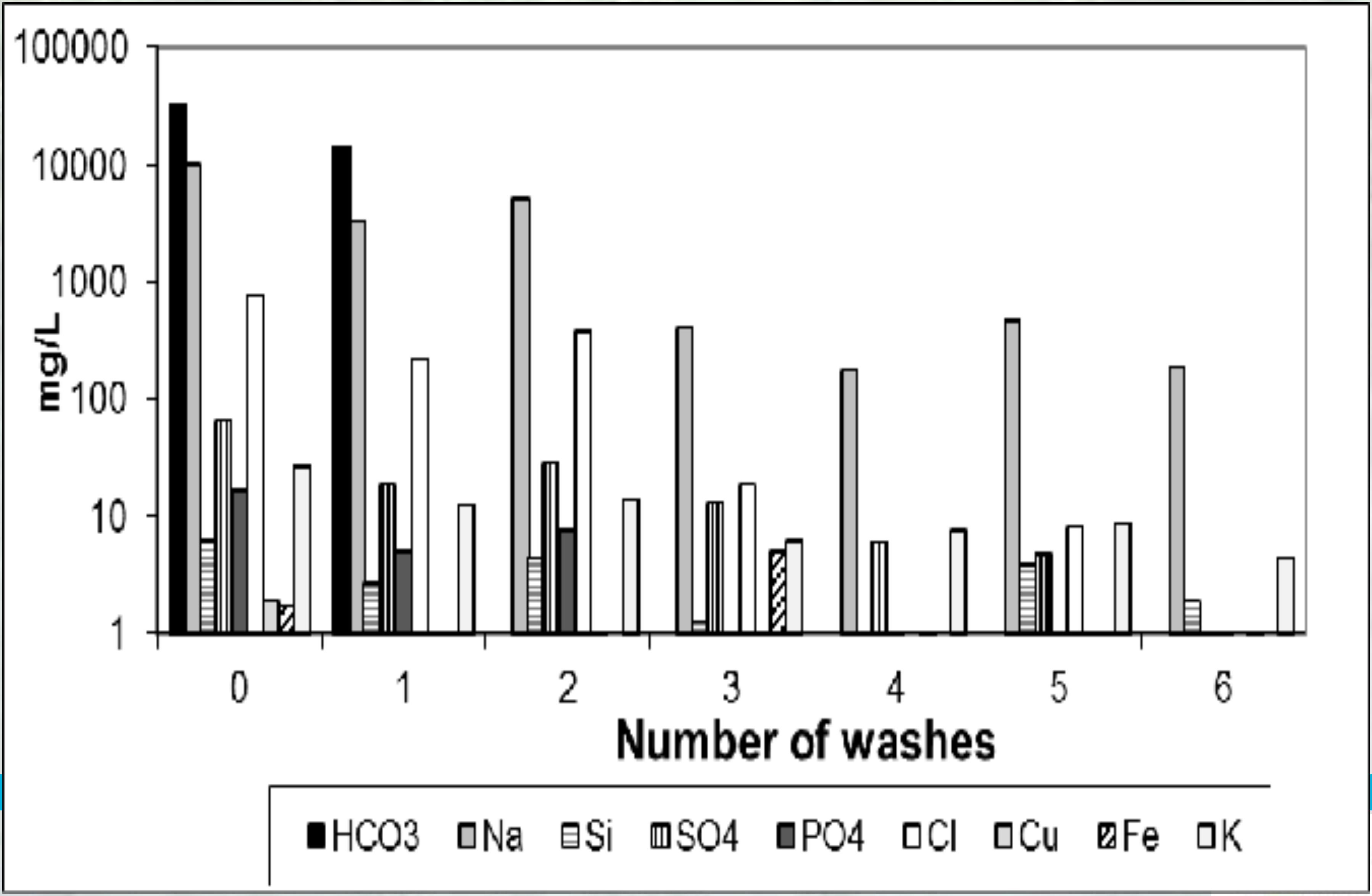
- ► Natural products were used as a source for deep eutectic solvents and ionic liquids.
- ► We define own chemical and physical properties of natural deep eutectic solvents.
- ► Interaction between natural deep eutectic solvents and solutes was confirmed by NMR.
- ► The developed natural deep eutectic solvents were applied as green media.

GRAPHICAL ABSTRACT



rie, API)

Purity of ice crystals ex EFC



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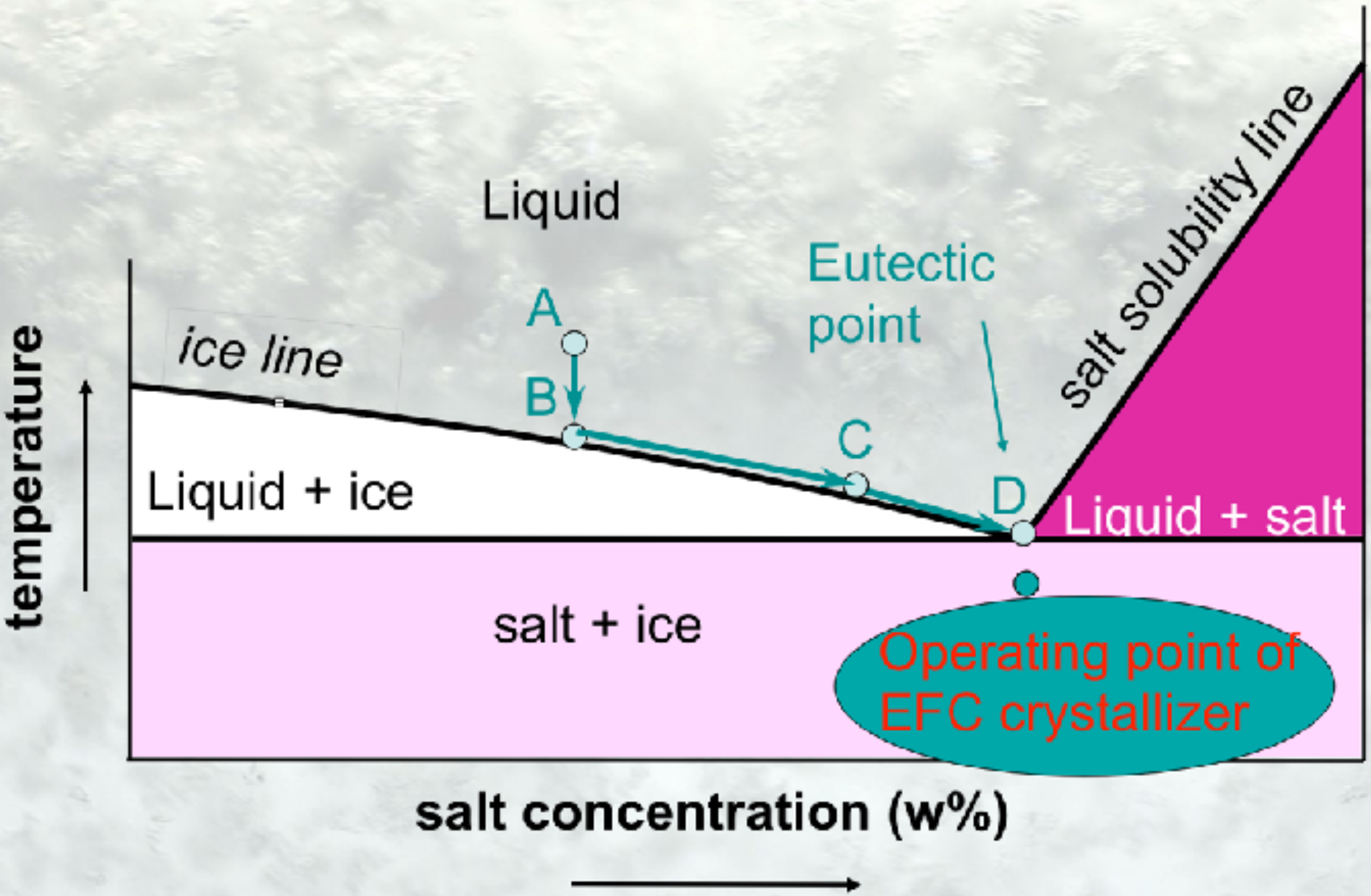
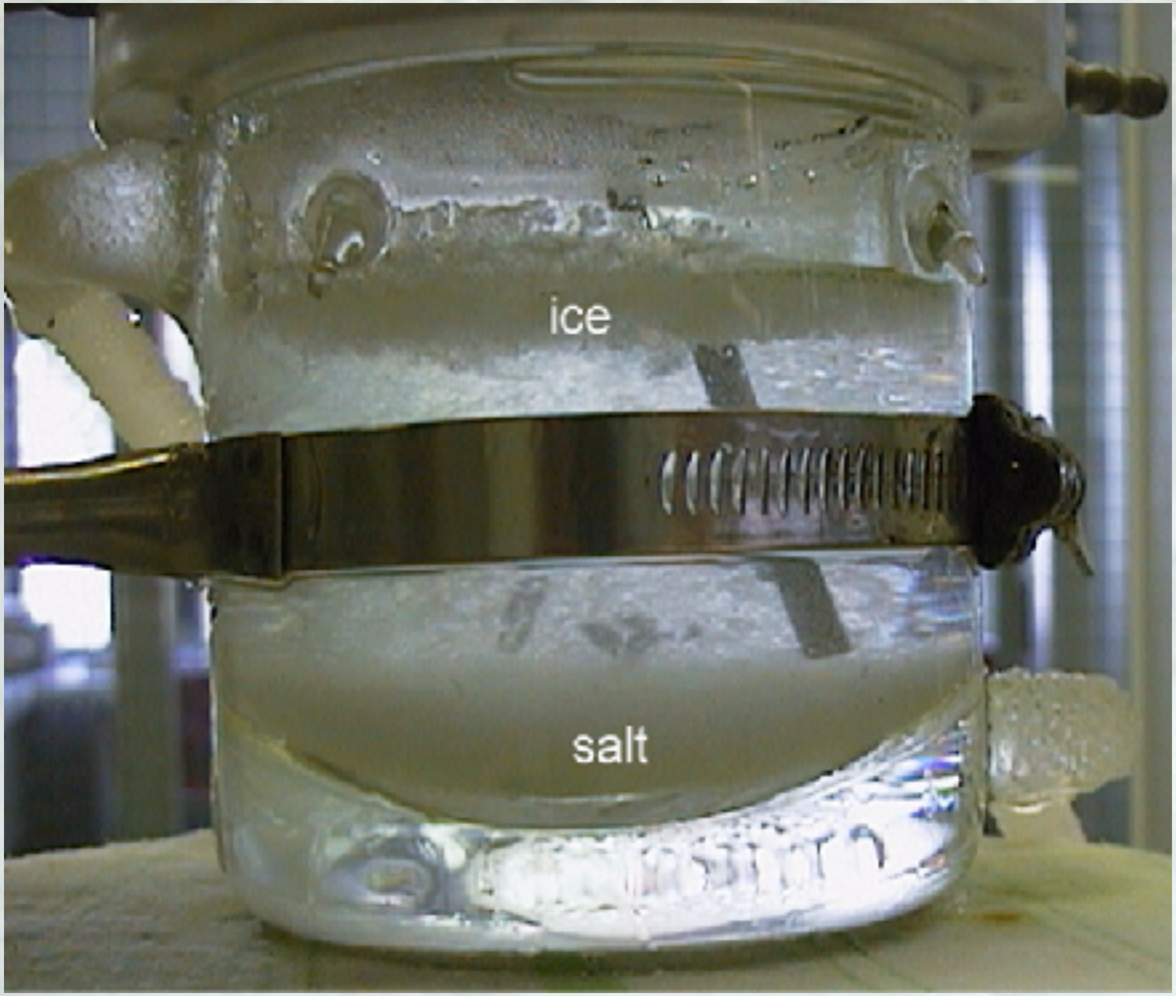
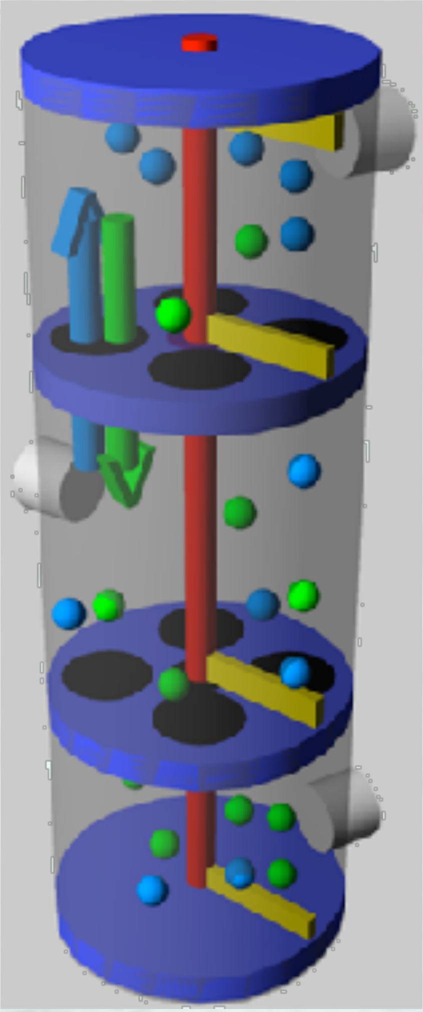

Liquid
Eutectic
point
salt solubility line
A
B
C
D
ice line
Liquid + ice
Liquid + salt
salt + ice
Operating point of
EFC crystallizer
temperature
salt concentration (w%)

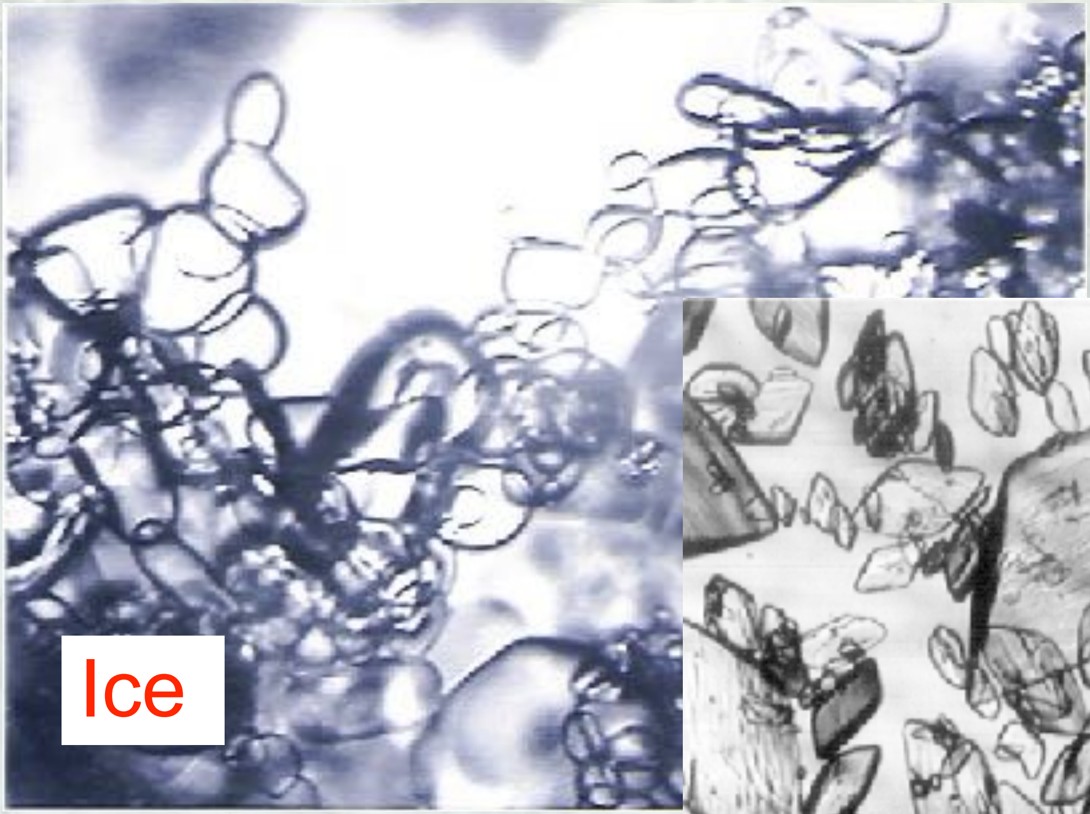
TUDelft

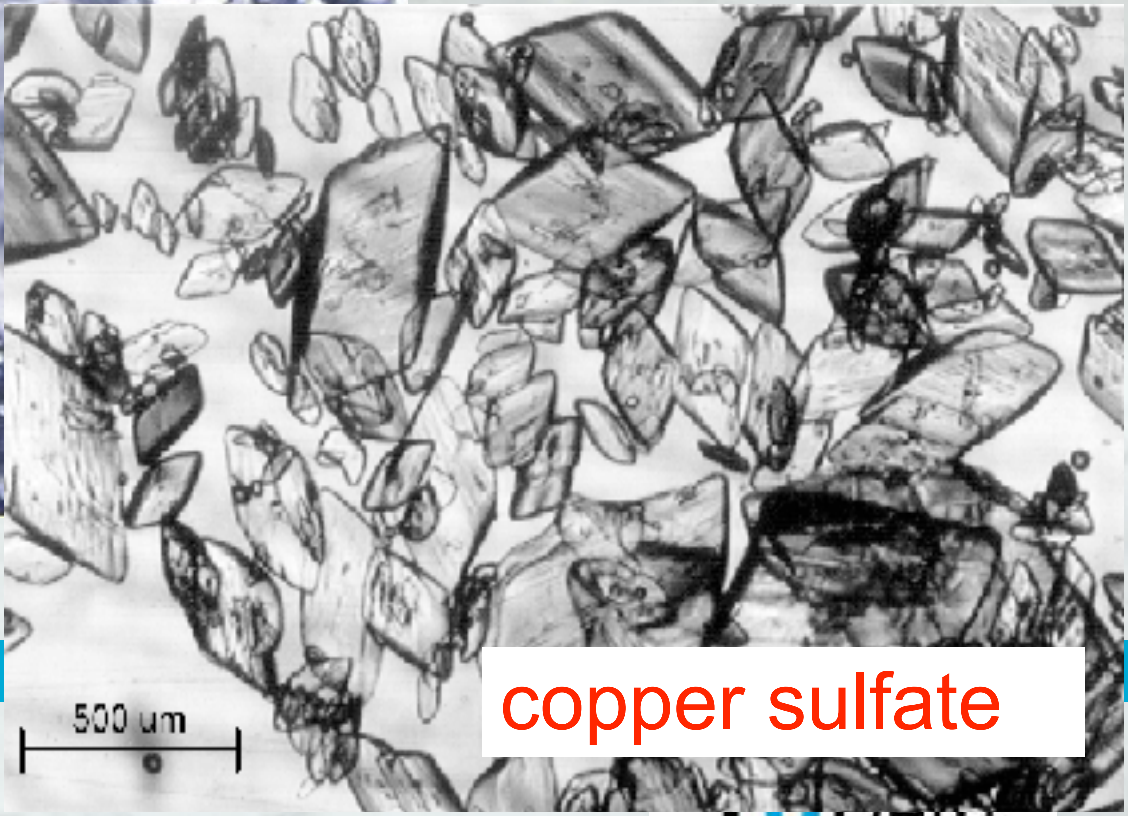
EFC separation of ice and salt crystals



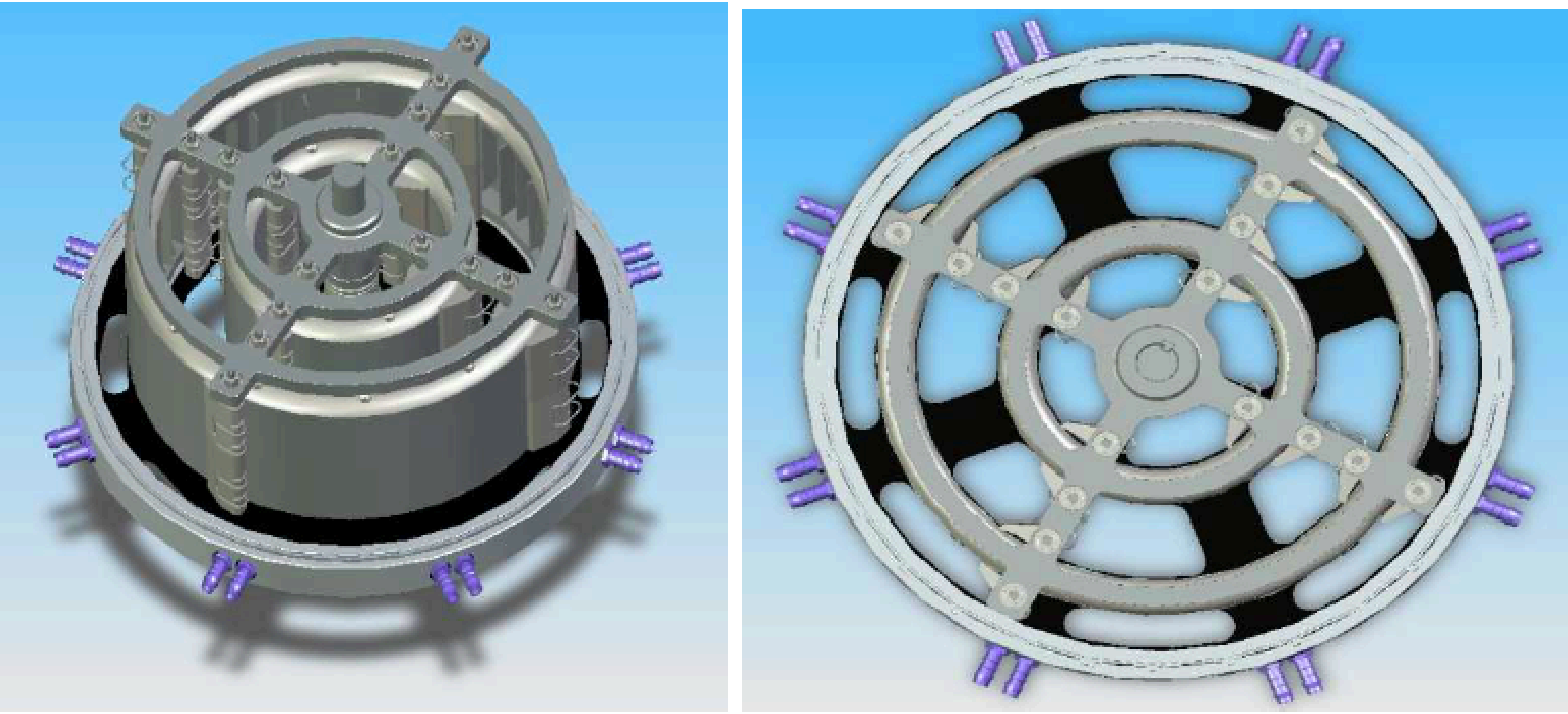


Simultaneous formation of ice and salt





Eutectic Freeze Crystalliser with KNO3 and ice



ıre 2. *Side and top view of the heat exchanger*

TUDelft

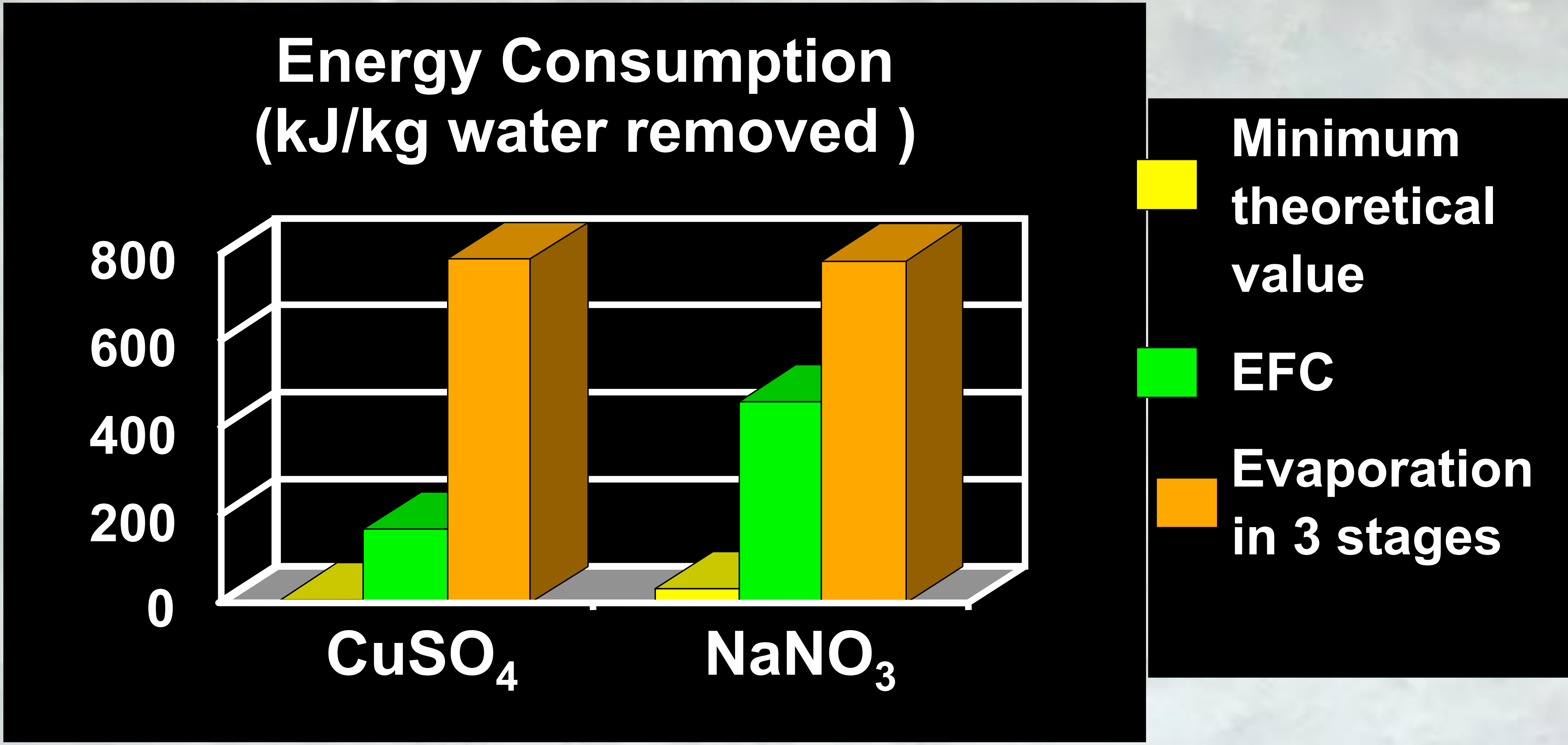
EFC at Nedmag ($MgSO_4$)

EFC properties

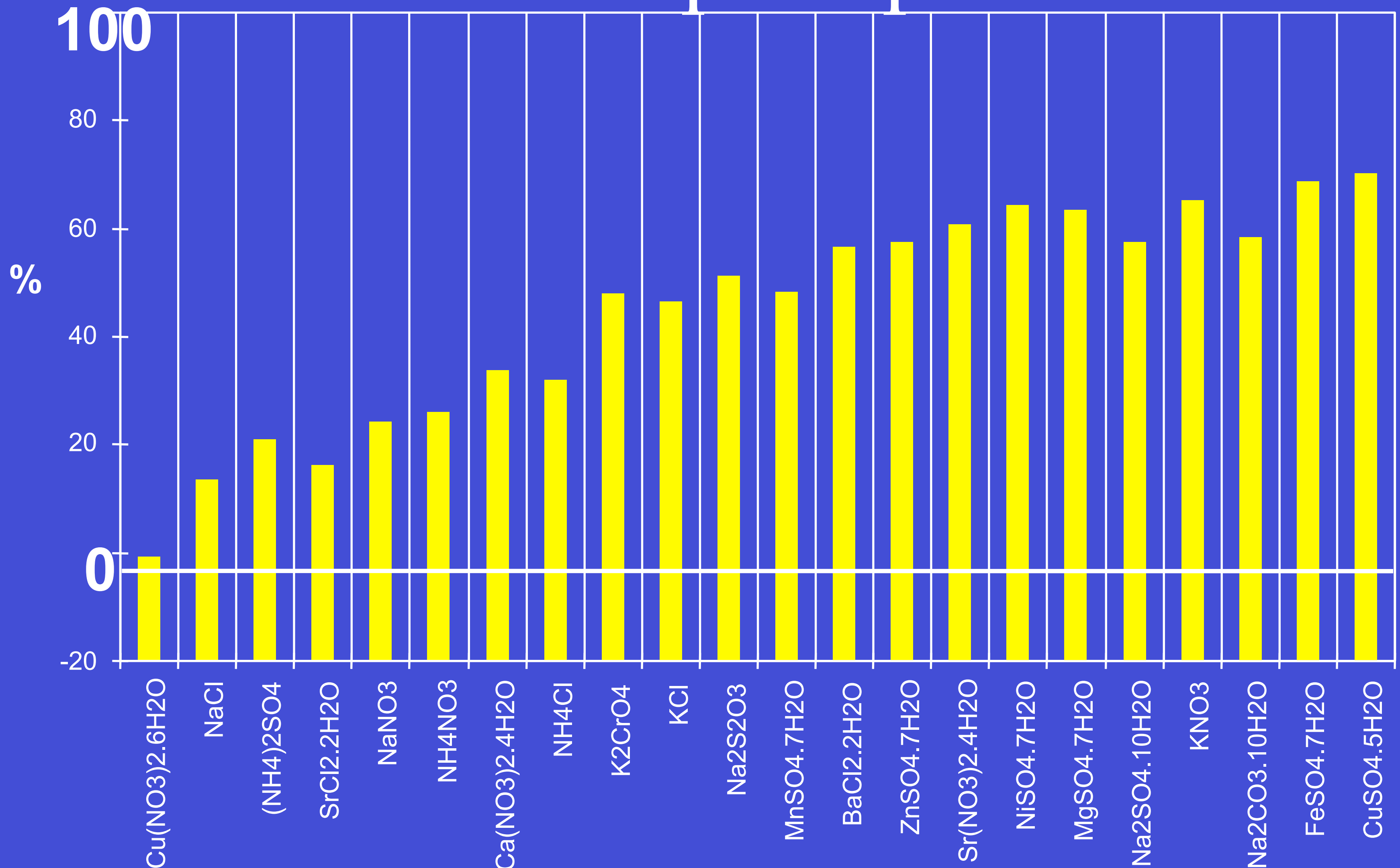
Also for highly concentrated streams (complementory to Reverse Osmosis)

- 100% yield theoretically (contrary to cooling crystallisation)
- Very high purity of water
- Salt purity high due to inherent low supersaturation (compared to evaporation)
- Up to 90% lower energy costs compared to single stage evaporation, up to 50% compd to triple stage (20% estd for NaCl).

Energy efficiency of complete salt-water separation (equal basis comparison)



Energy savings EFC compared to 3-step evap.



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