SOLVENT SELECTION AND DESIGN FOR

(BIO)REFINERY APPLICATIONS

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Biorefinery & Circular Economy

Perspective & Challenges

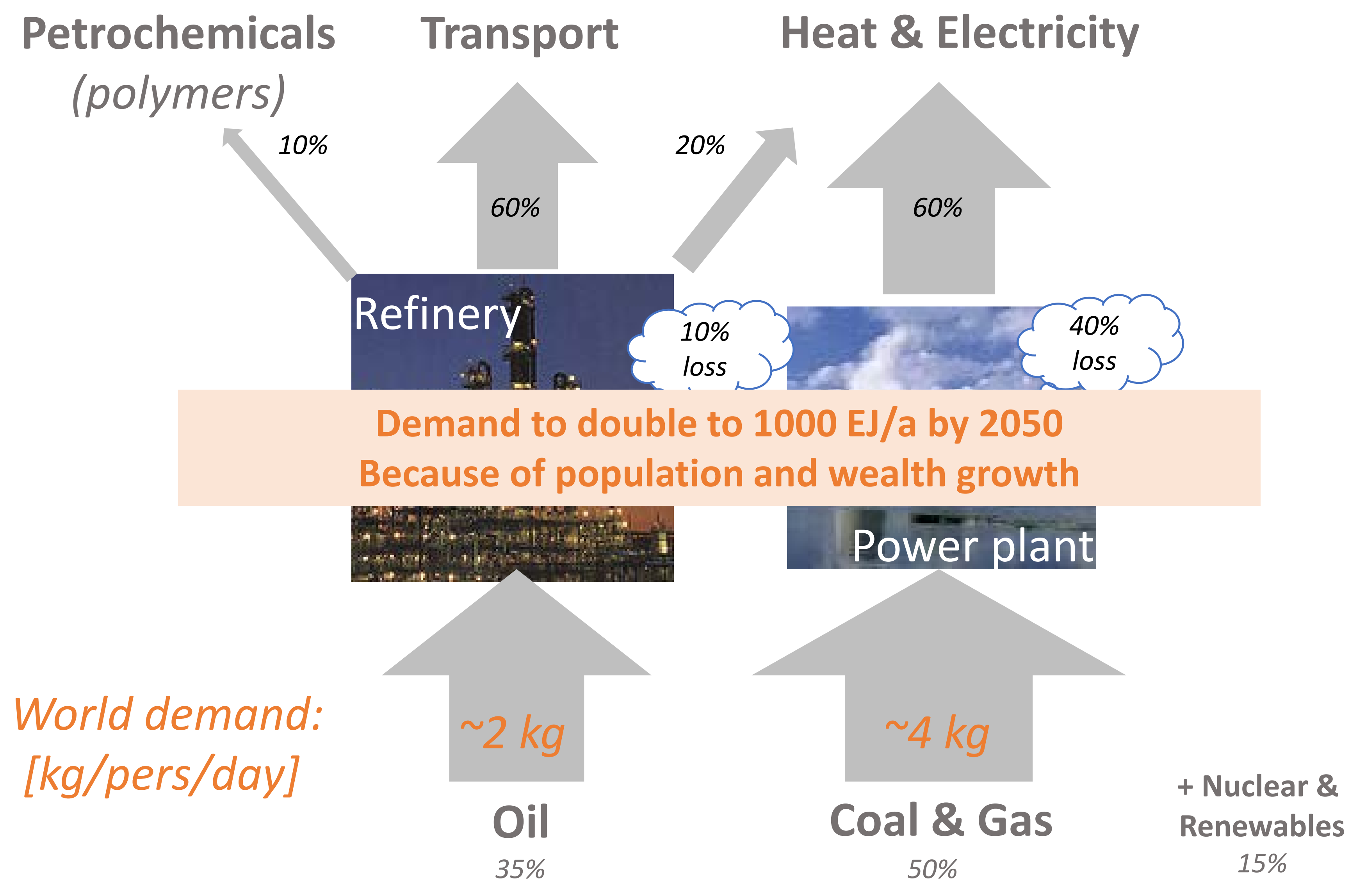
Examples liquid-liquid extraction applications

Fractionation of pyrolytic bio-oils

Volatile Fatty Acid recovery from fermented wastewater

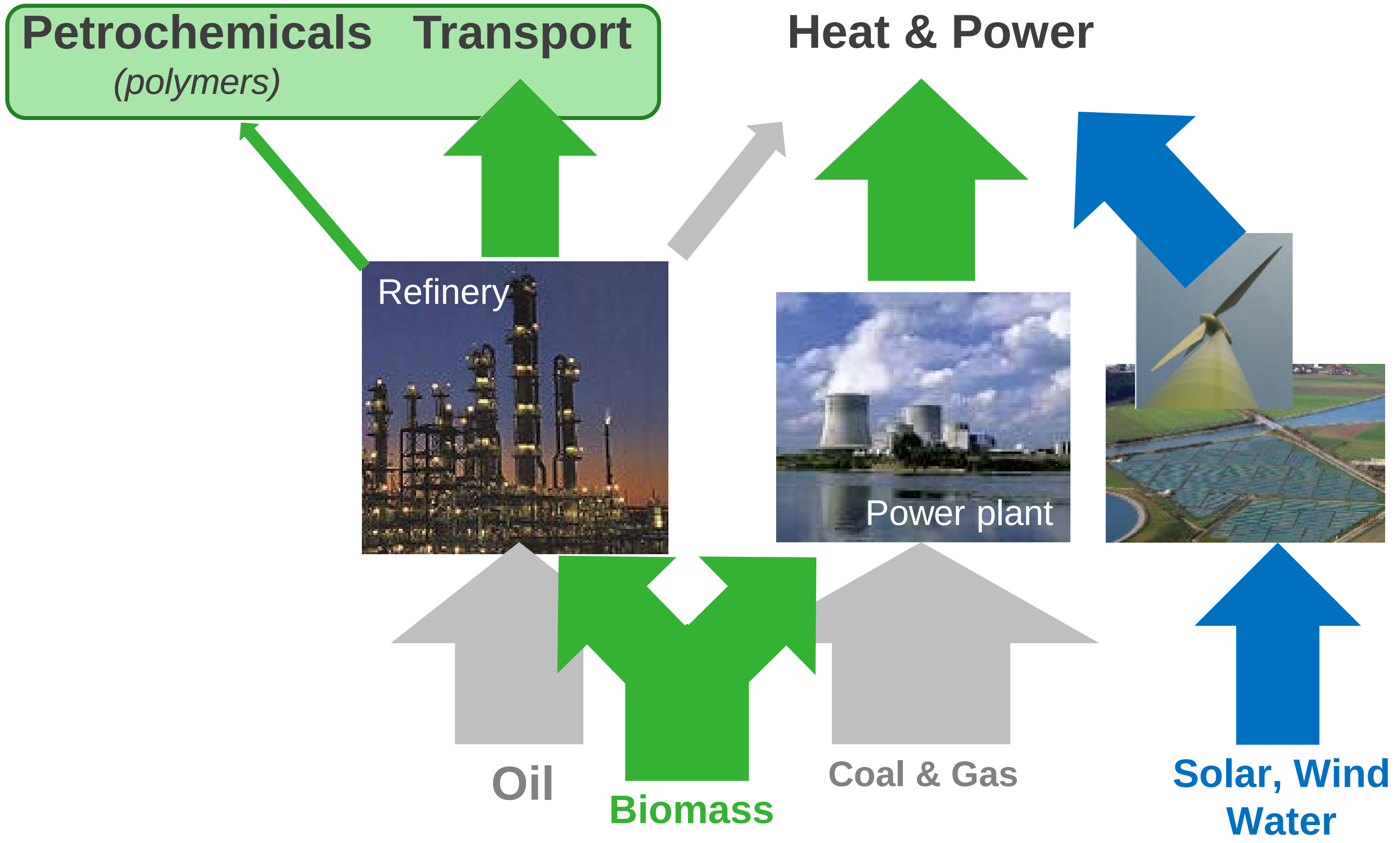
Conclusions and outlook

IL APPLICATIONS IN BIOREFINERY
The topics



Lange, 2015

FOSSIL ENERGY DEMAND
500 EJ PER YEAR

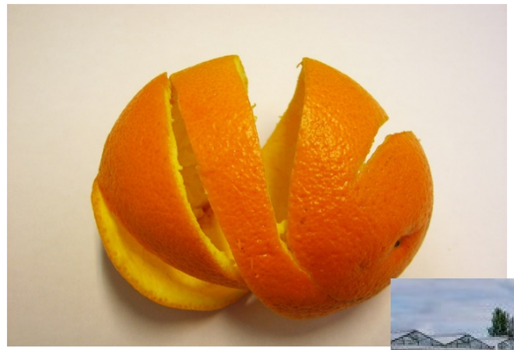


Lange, 2015

SUSTAINABLE ALTERNATIVES
Biomass refining essential

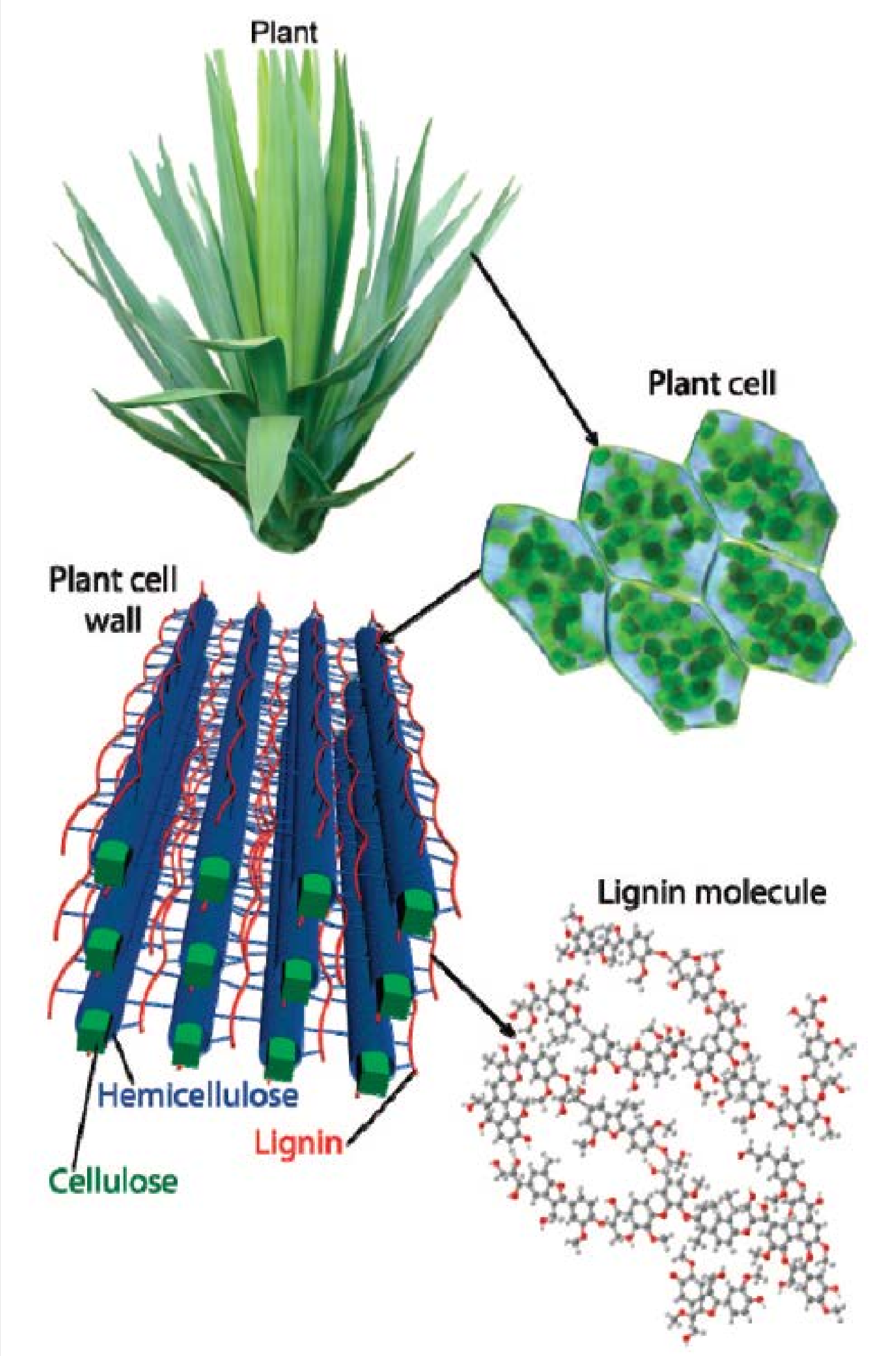
THE BIOREFINERY CONCEPT

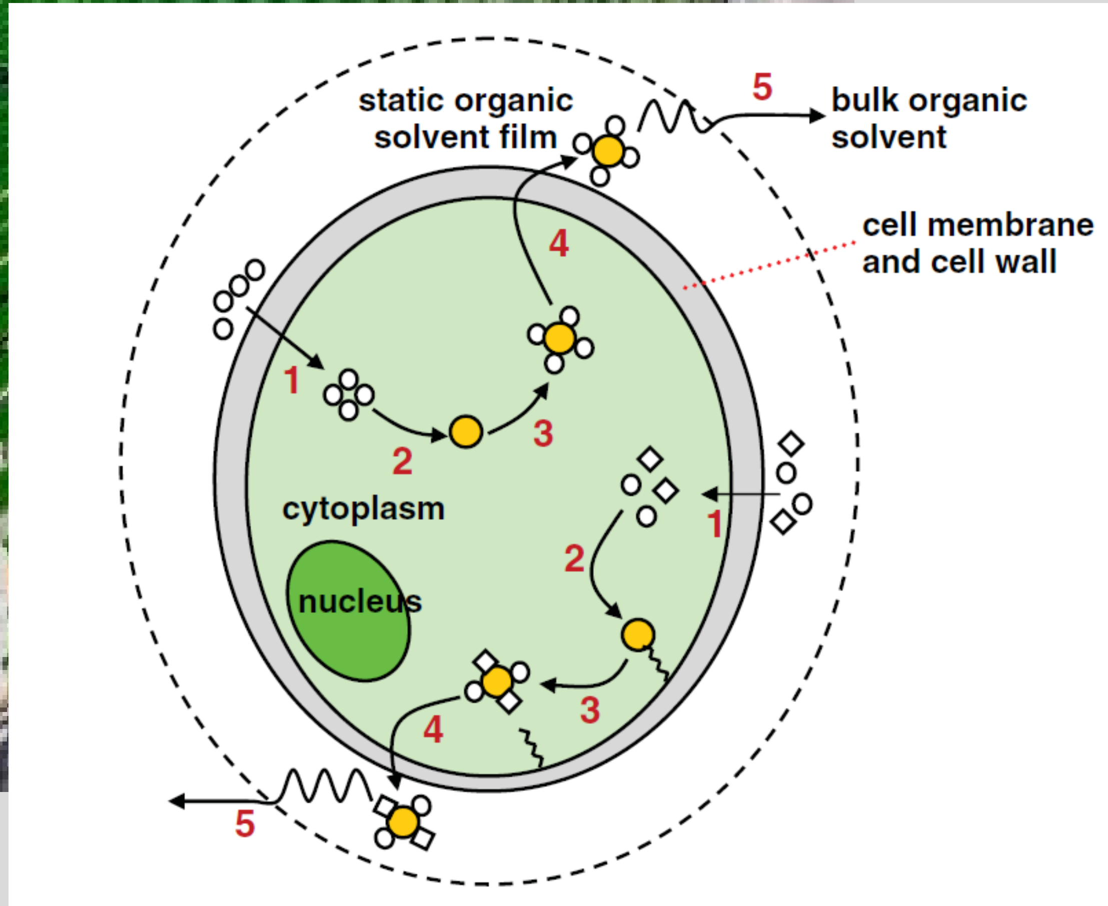
Separation technology is key enabler



biorefinery →

- fuels
- solvents
- bulk chemicals
- plastics
- fibers
- fine chemicals





Weckhuysen et al, Chem Rev 2010 110 3552

AlgaePARC

Halim et al, Biotechnol Adv 2012 30 709

BIOMASS
a complex matrix

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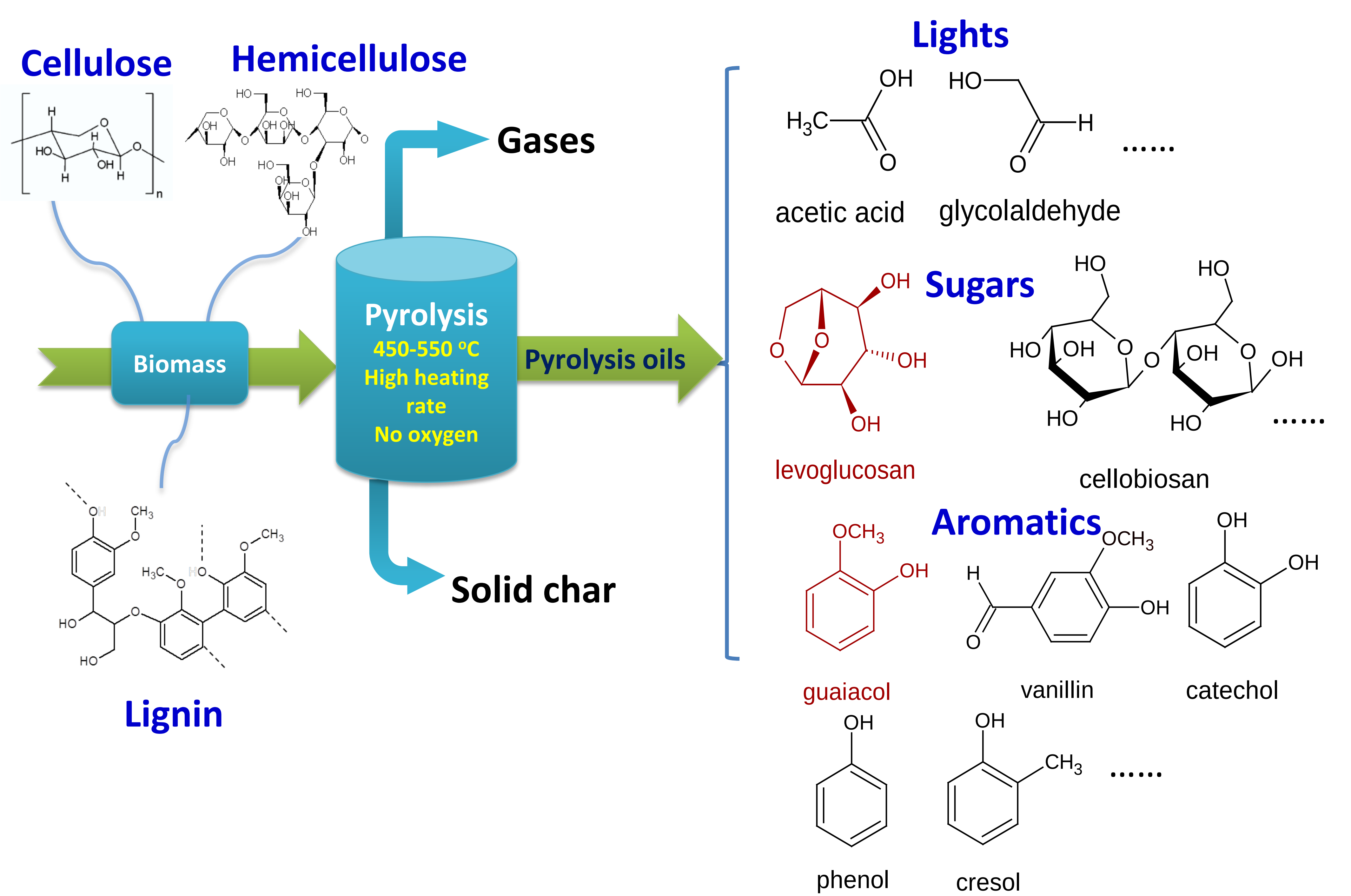


BIOMASS VALORIZATION APPROACHES
Pyrolysis – destructive method

All polymers break down

Many secondary reactions

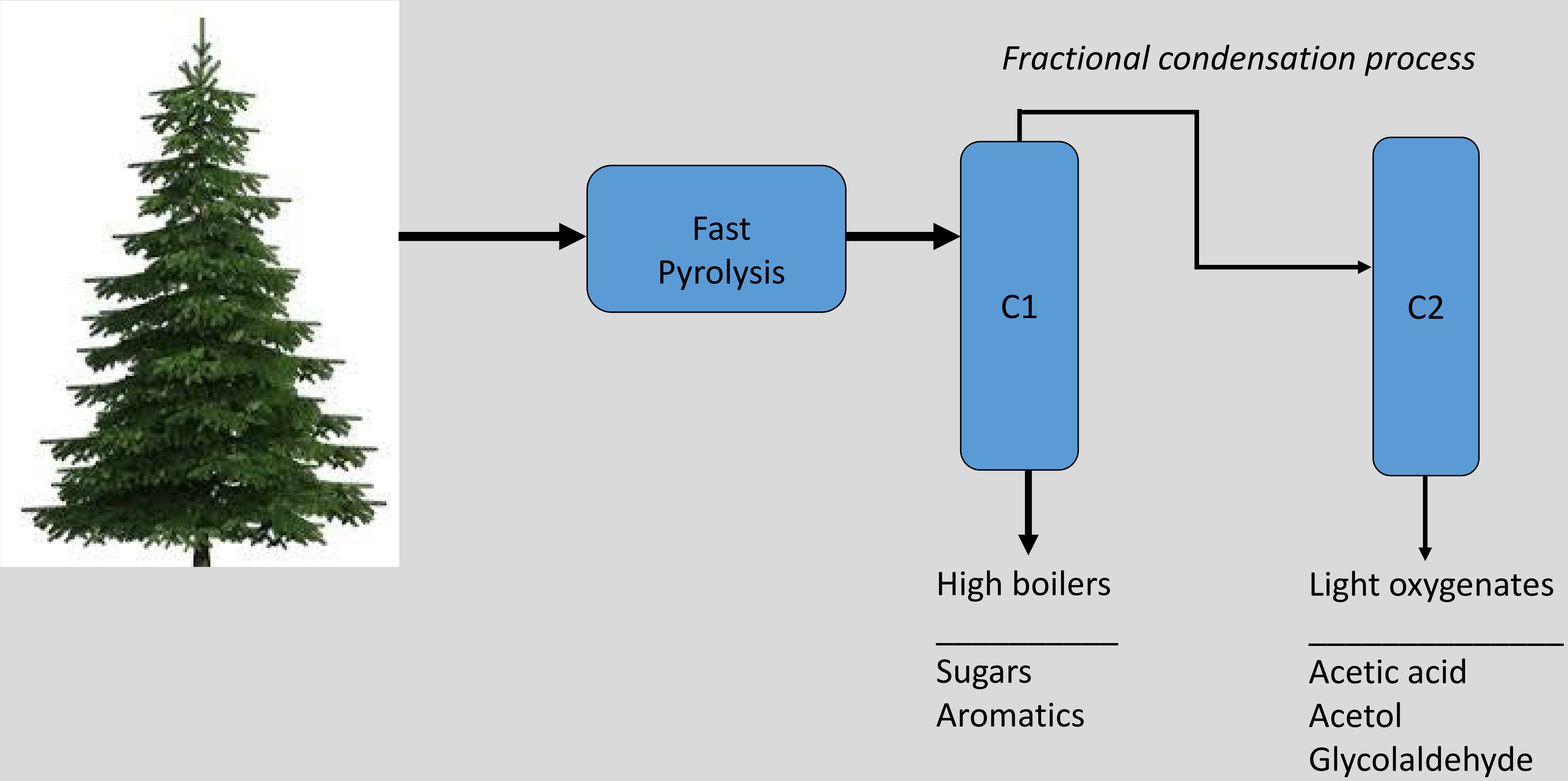
Many small molecules

Very complex liquid

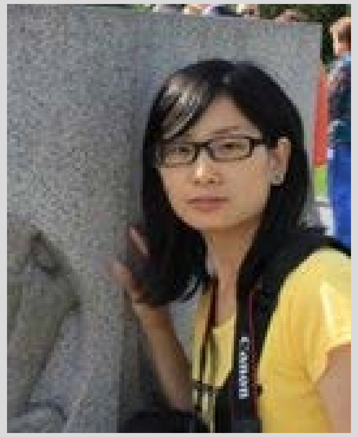
Valuables:
aromatics, sugars, lights

DOWNSTREAM SEPARATION CHALLENGES!!

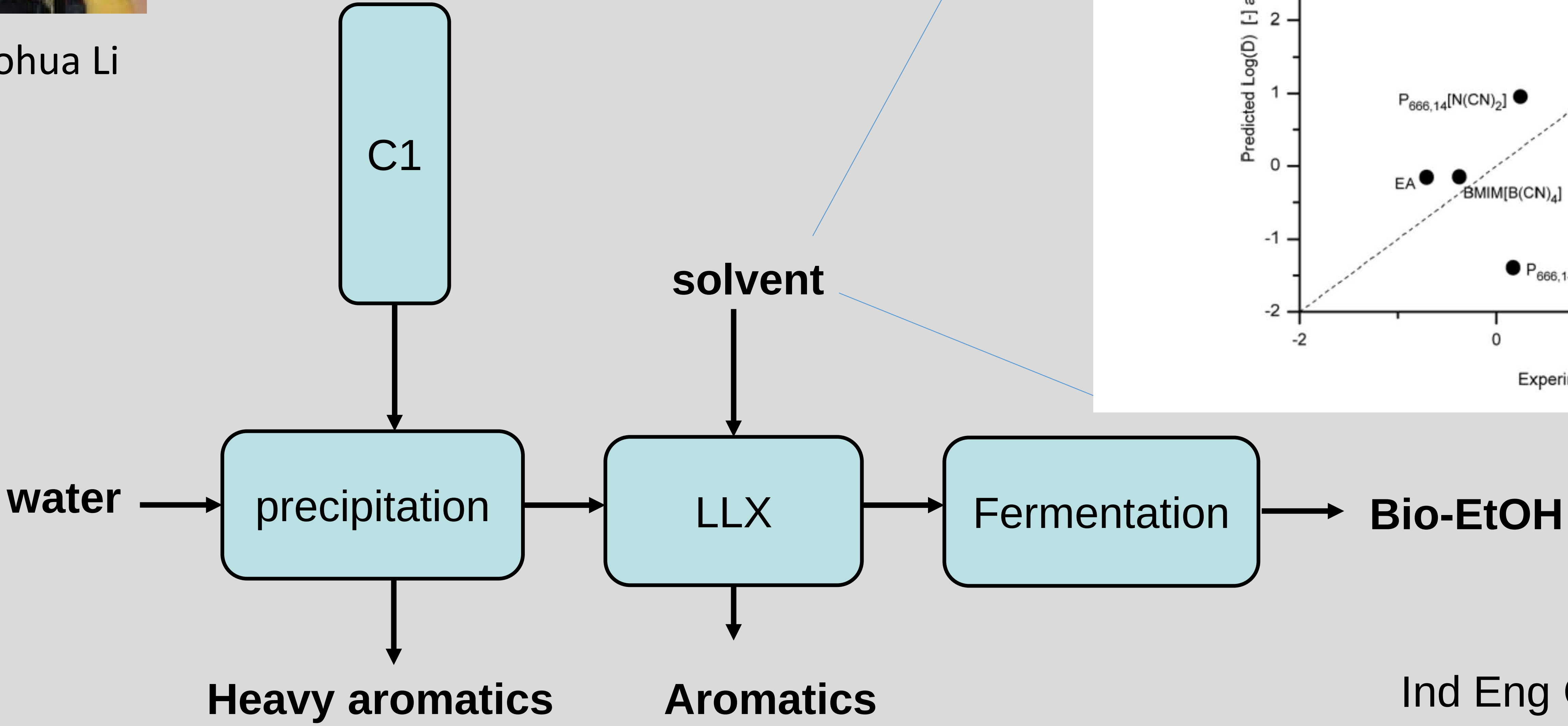
Schuur et al,
Sep Purif Technol 2017 175 498
Biores Technol 2016 216 12
Ind Eng Chem Res 2016 55 4703

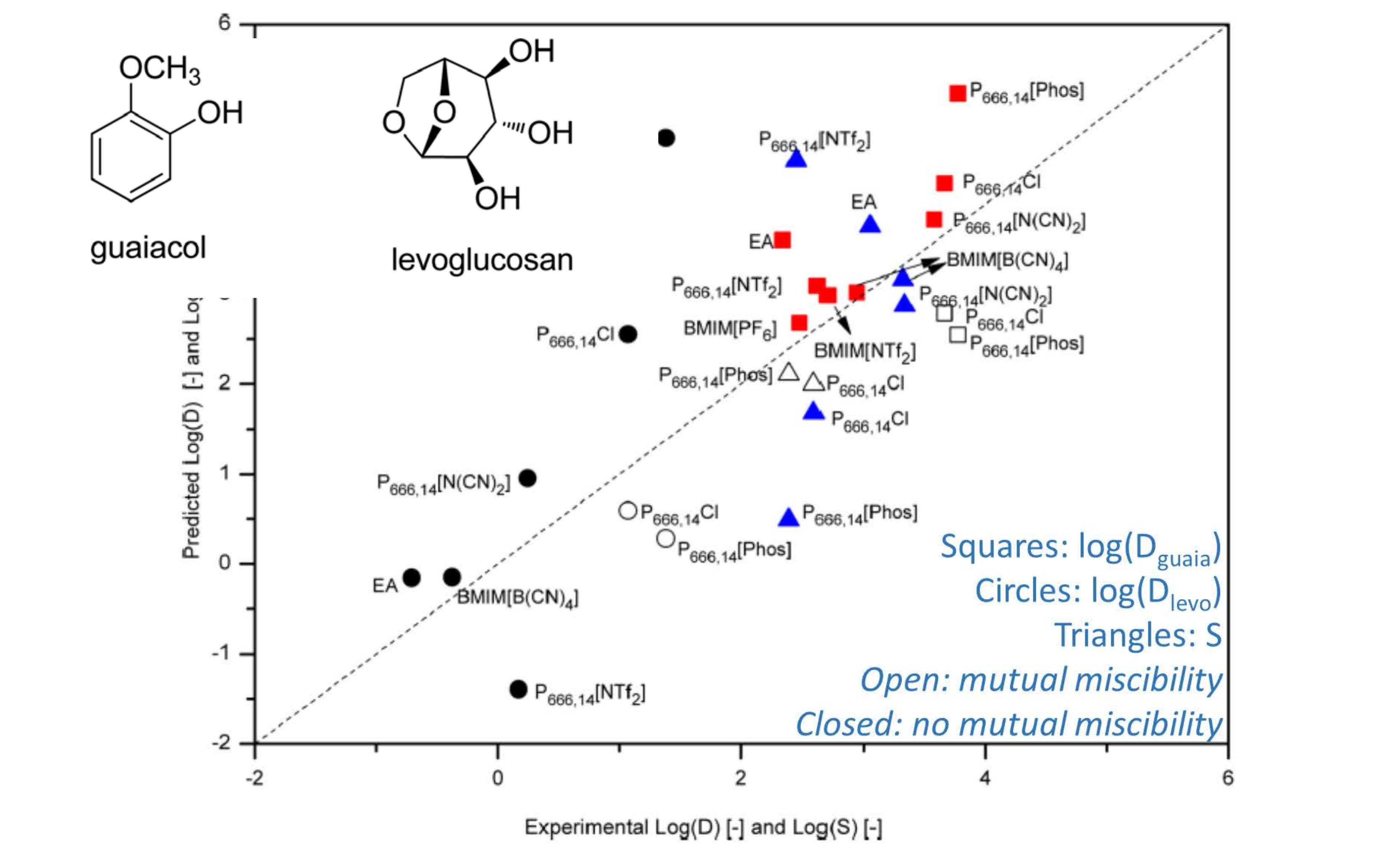


PYROLYSIS OIL STUDIES
COSMO-RS + model system + real system



Xiaohua Li

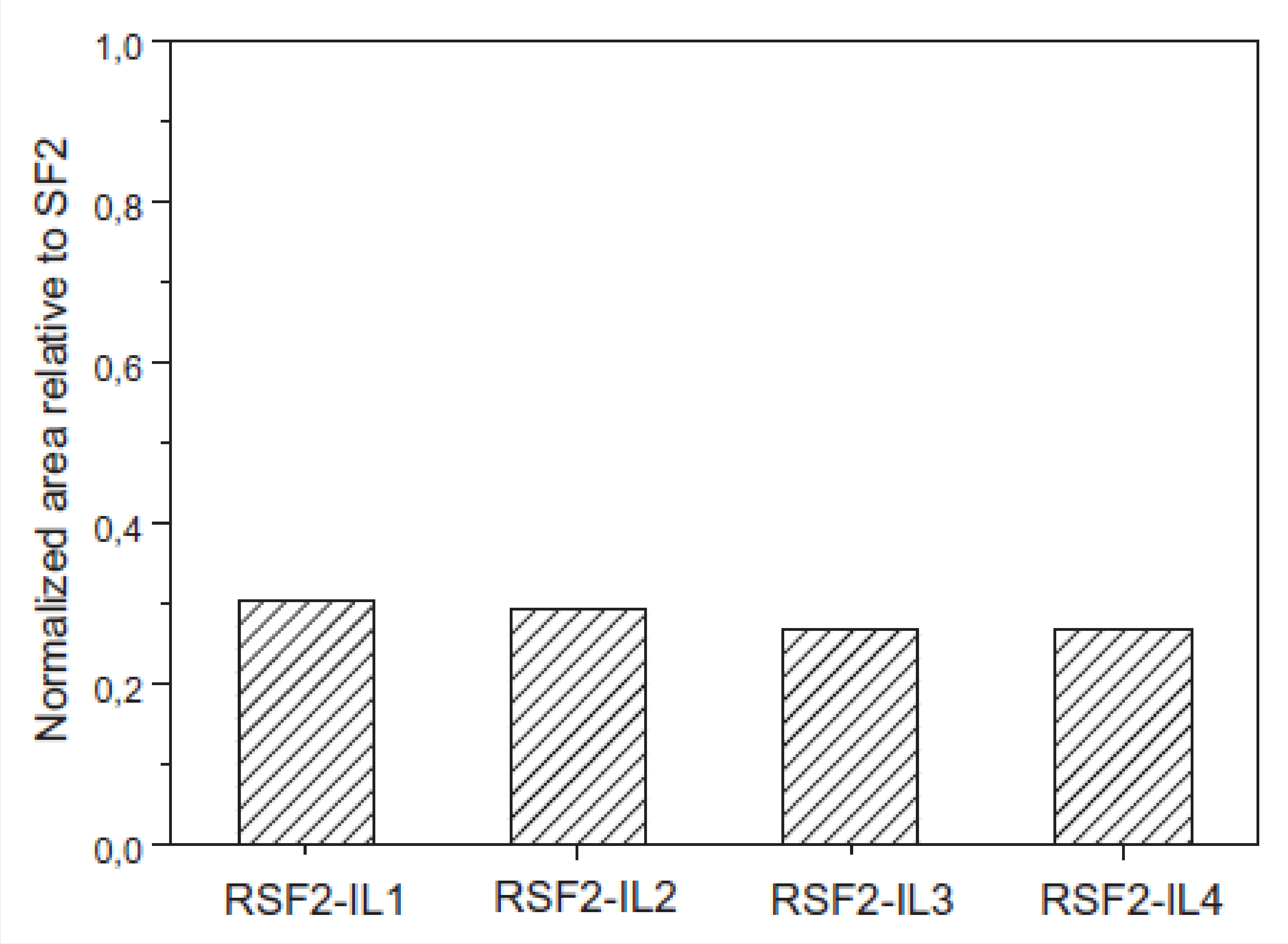




$[P_{666,14}][N(CN)_2]$ most promising

Ind Eng Chem Res 2016 55 4703-4710

FIRST CONDENSER OIL TREATMENT
Separating aromatics and sugars



Biores Technol 2016 216 12-18

$[P_{666,14}][N(CN)_2]$ from screening study

Stable operation with real oil

Multiple regenerations proven

Also estimates on energy use made

IL based process = EA based / 5

Ind Eng Chem Res 2016 55 4703-4710

THE REAL PYROLYSIS OIL
Extraction + regeneration 4 times

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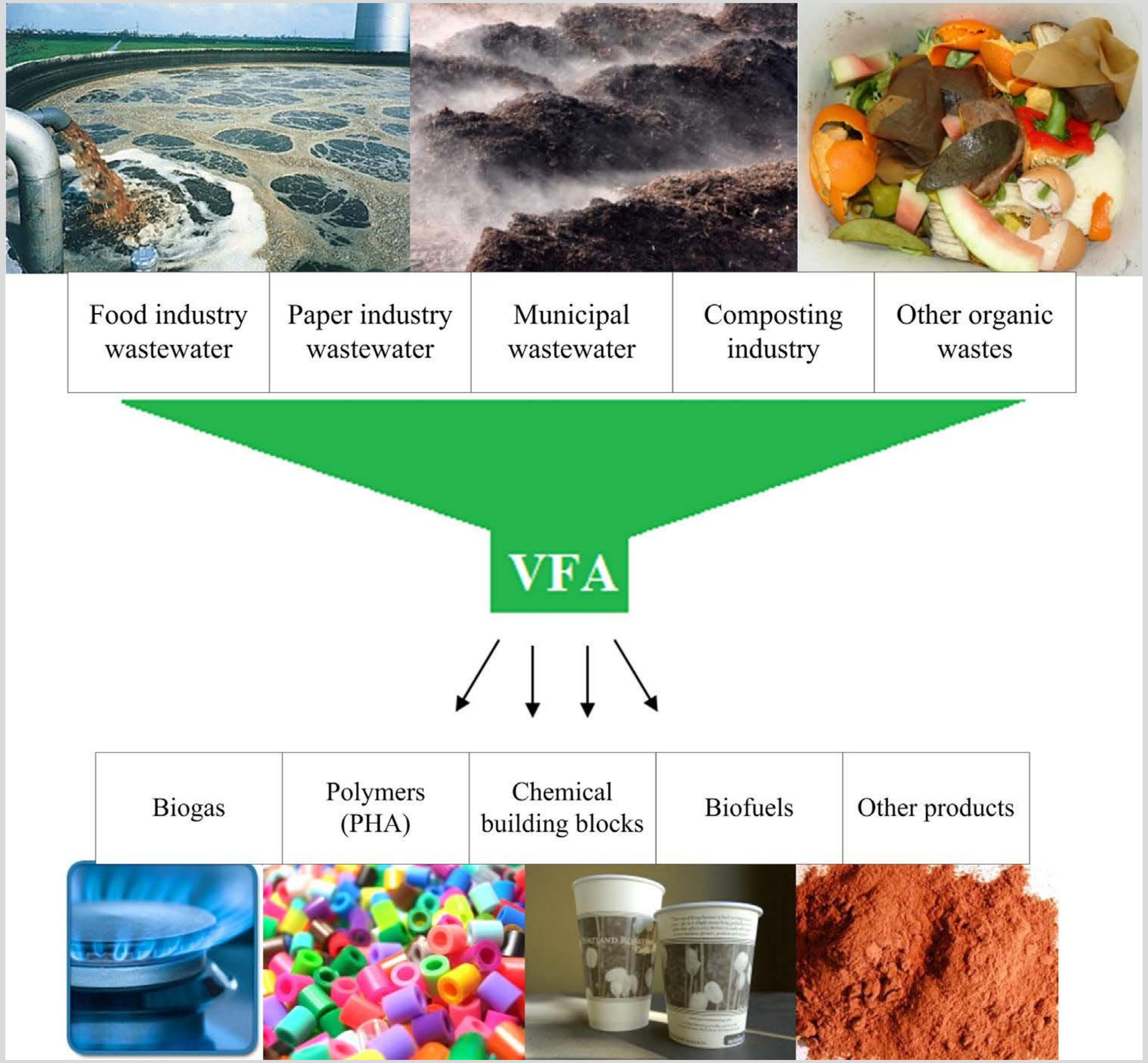


Kleerebezem et al, Biotech Bioeng 2015 112 2248

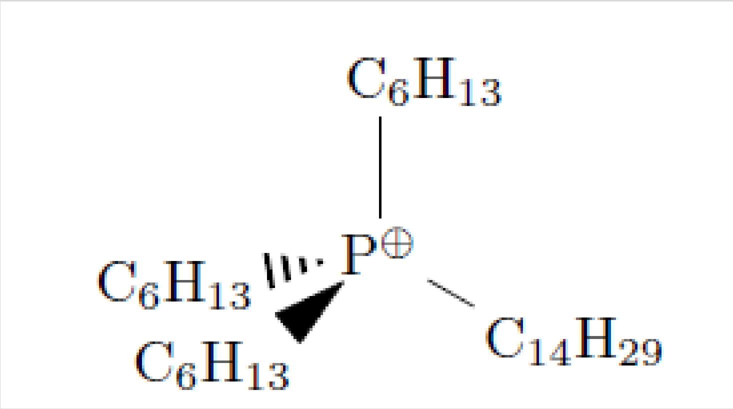
Typical composition of fermented wastewater.

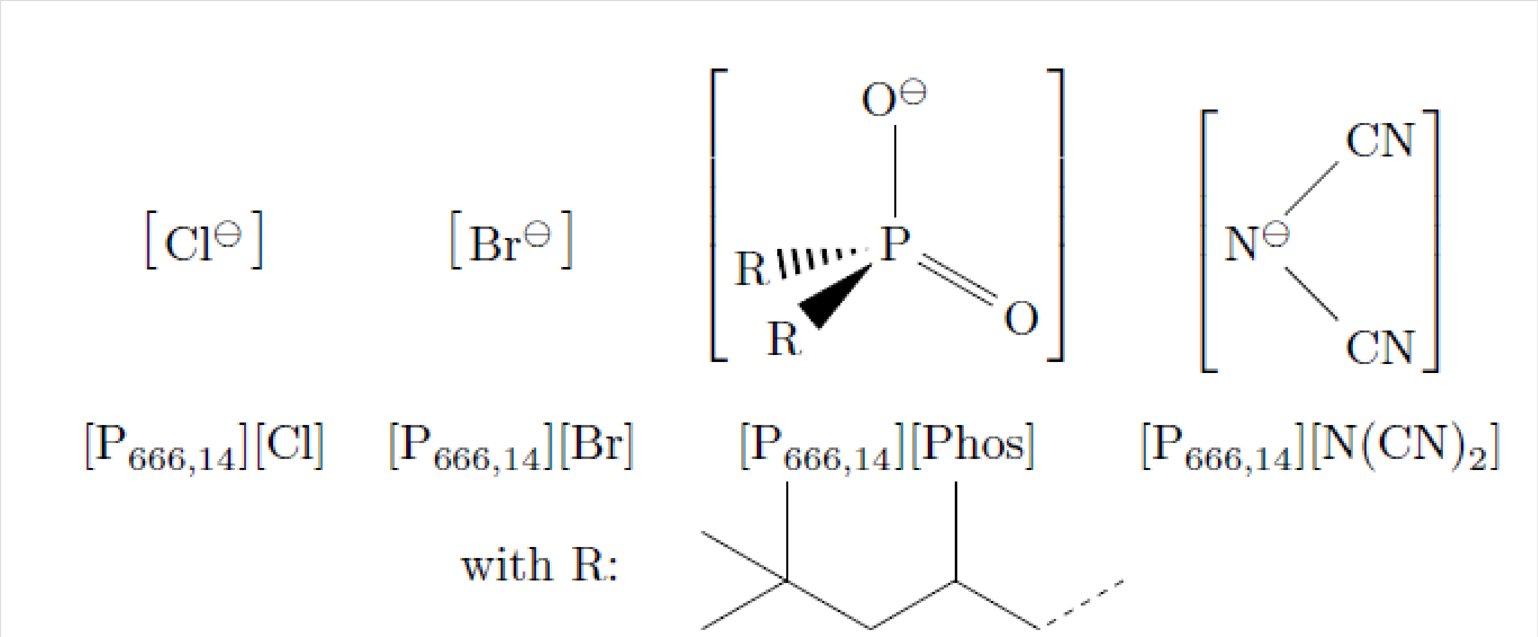
Component	Chemical formula	Concentration (g/L)
Acetic acid	CH_3COOH	2.5–10
Propionic acid	CH_3CH_2COOH	2.5–10
Butyric acid	$CH_3(CH_2)_2COOH$	2.5–10
Lactic acid	$CH_3CH(OH)COOH$	2.5–10
Sodium	Na^+	1–5
Potassium	K^+	1–5
Chloride	Cl^-	1–10
Phosphate	$H_2PO_4^-/HPO_4^{2-}$	1–10
Sulfate	SO_4^{2-}	1–10
Sulfide	S^{2-}	0.3
Magnesium	Mg^{2+}	0.3
Calcium	Ca^{2+}	0.3
Ammonium	NH_4^+	0.1
Trace elements (e.g. cobalt, nickel and iron)	Co, Fe, Ni (ionic forms)	10^{-4}
Inert COD (e.g. humic acid and fulvic acid)		1
Microbes		

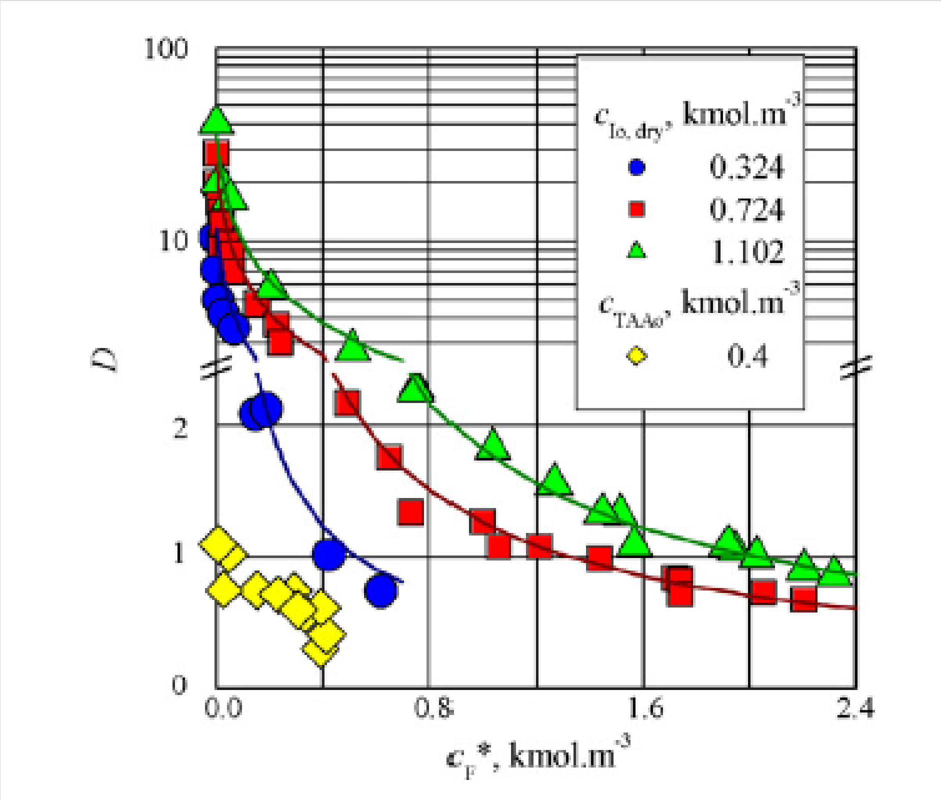
Schuur et al, Sep Purif Technol 2016 161 61

Ehsan Reyhanitash & Chiel v Beek

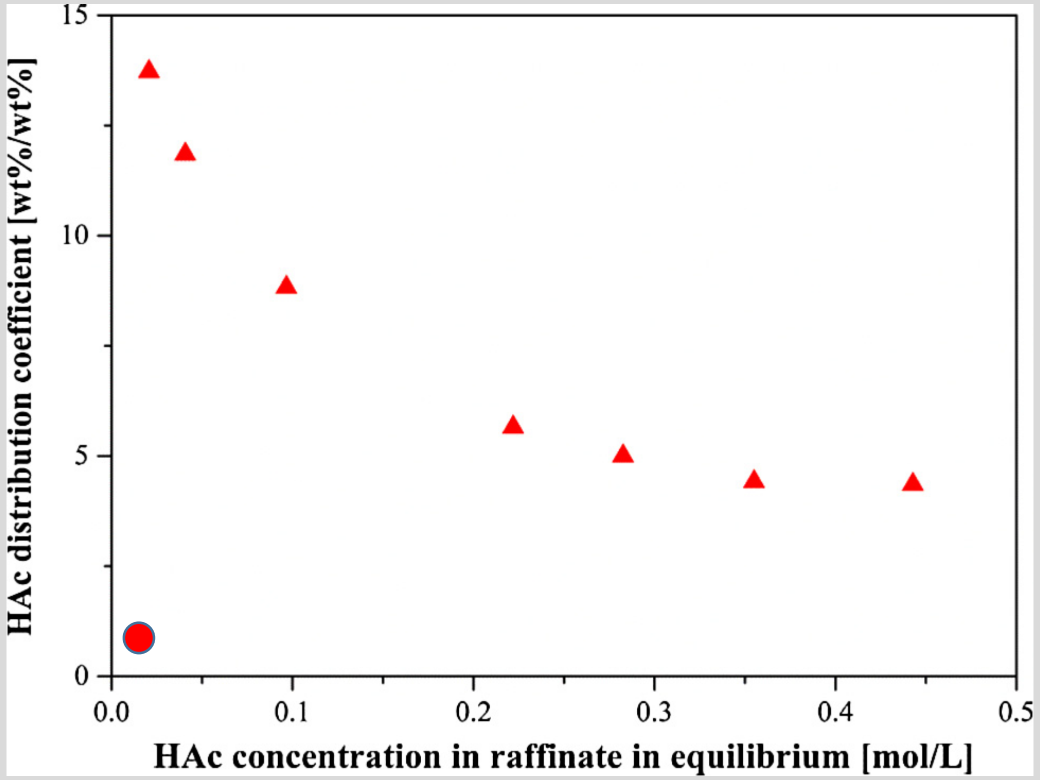
REFINING FERMENTED WASTEWATER
VFAs, valuable platform chemicals







Martak & Schlosser,
Sep Purif Technol 2007 57 483-494



Schuur et al, Sep Purif Technol 2016 161 61-68

RECENT LITERATURE ON LLX OF ACIDS
ILs perform much better than TOA at low C

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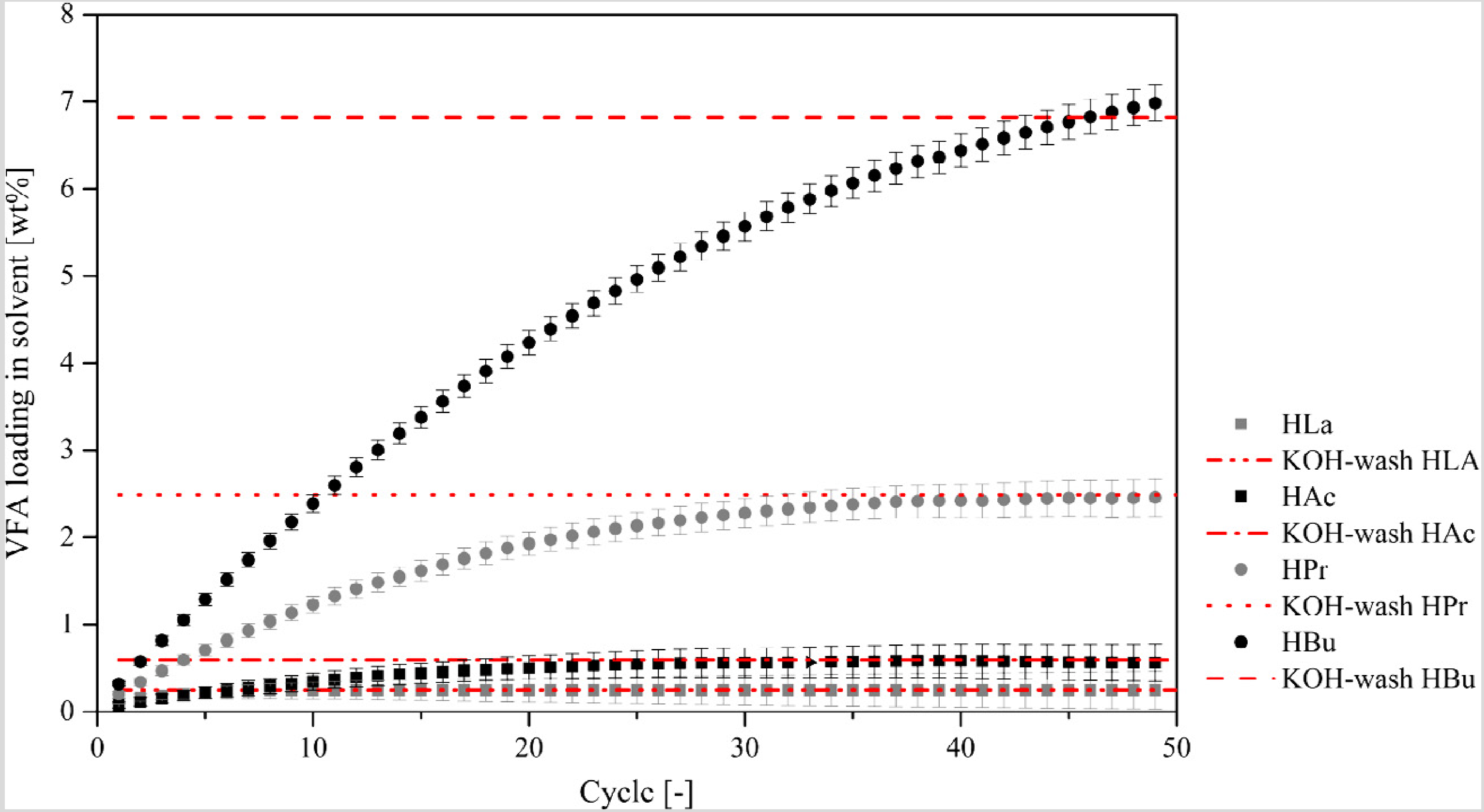

Schuur et al, Sep Purif Technol 2016 161 61-68

CROSS CURRENT MULTISTAGE LLX
Estimate max loading $(S/F)_{min}$

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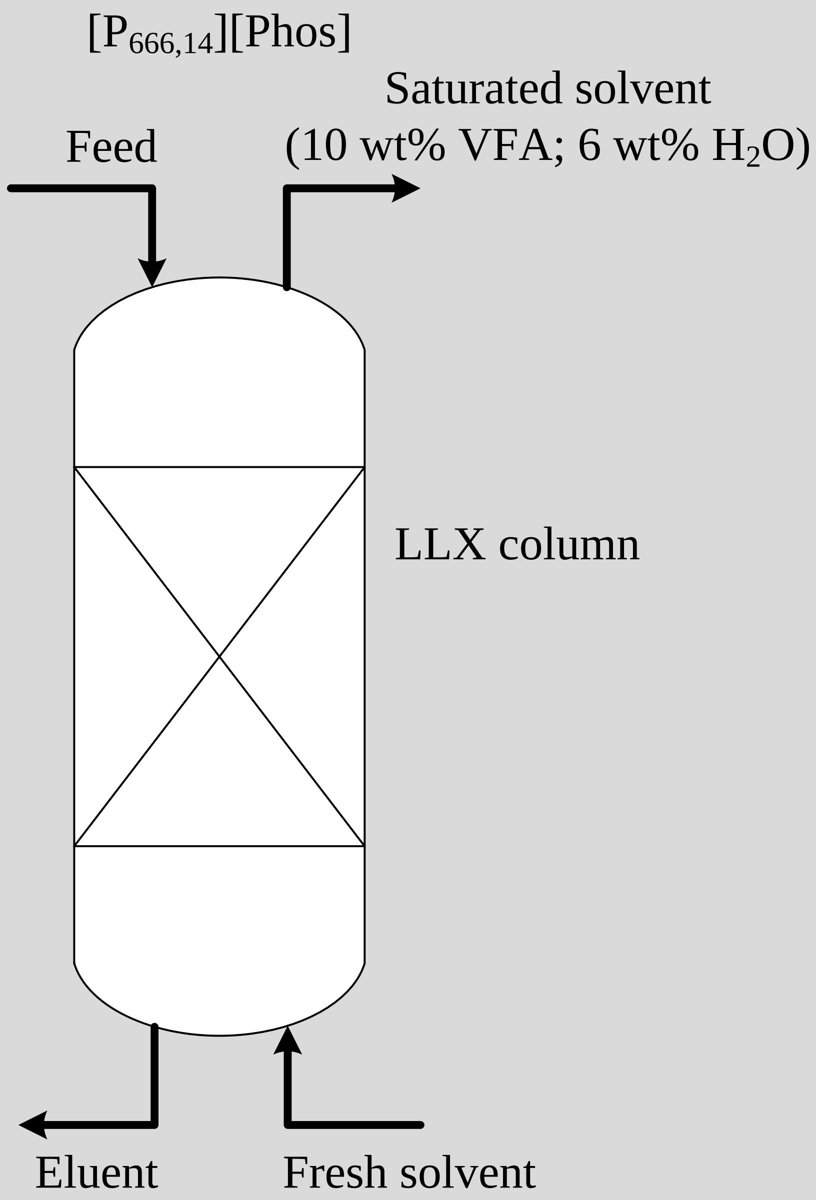
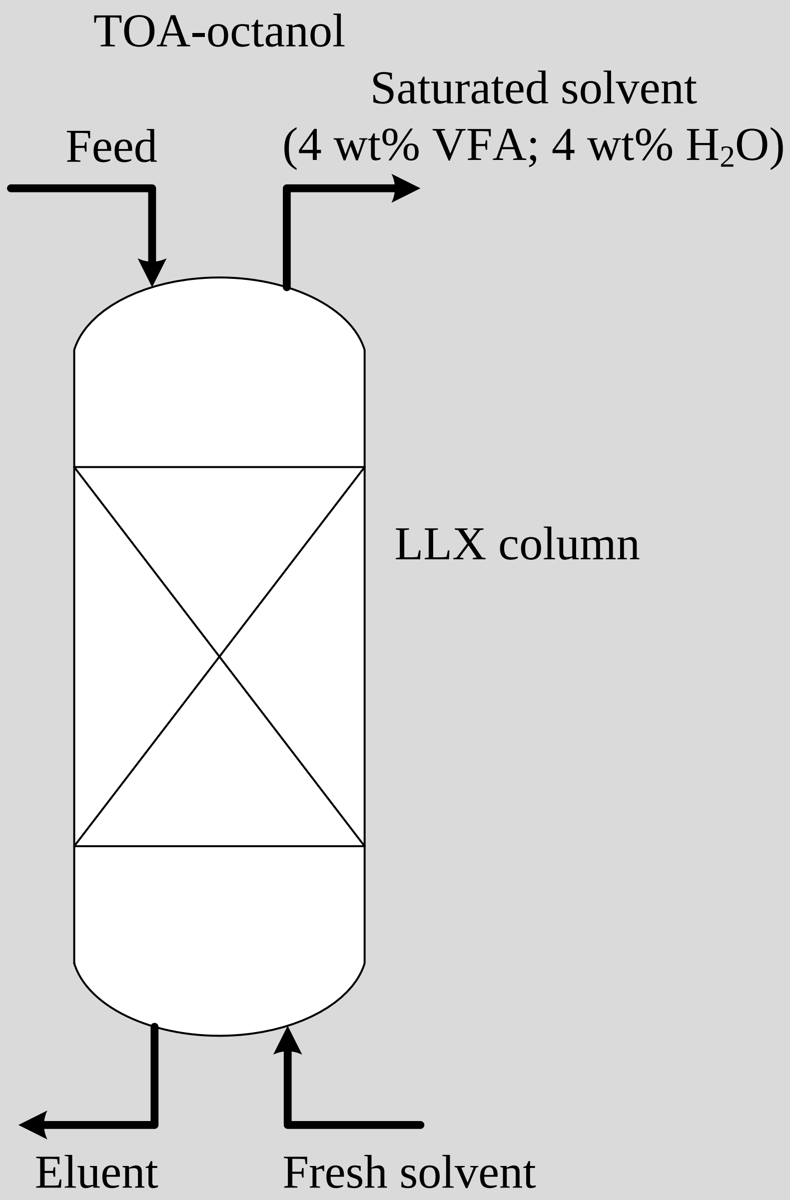
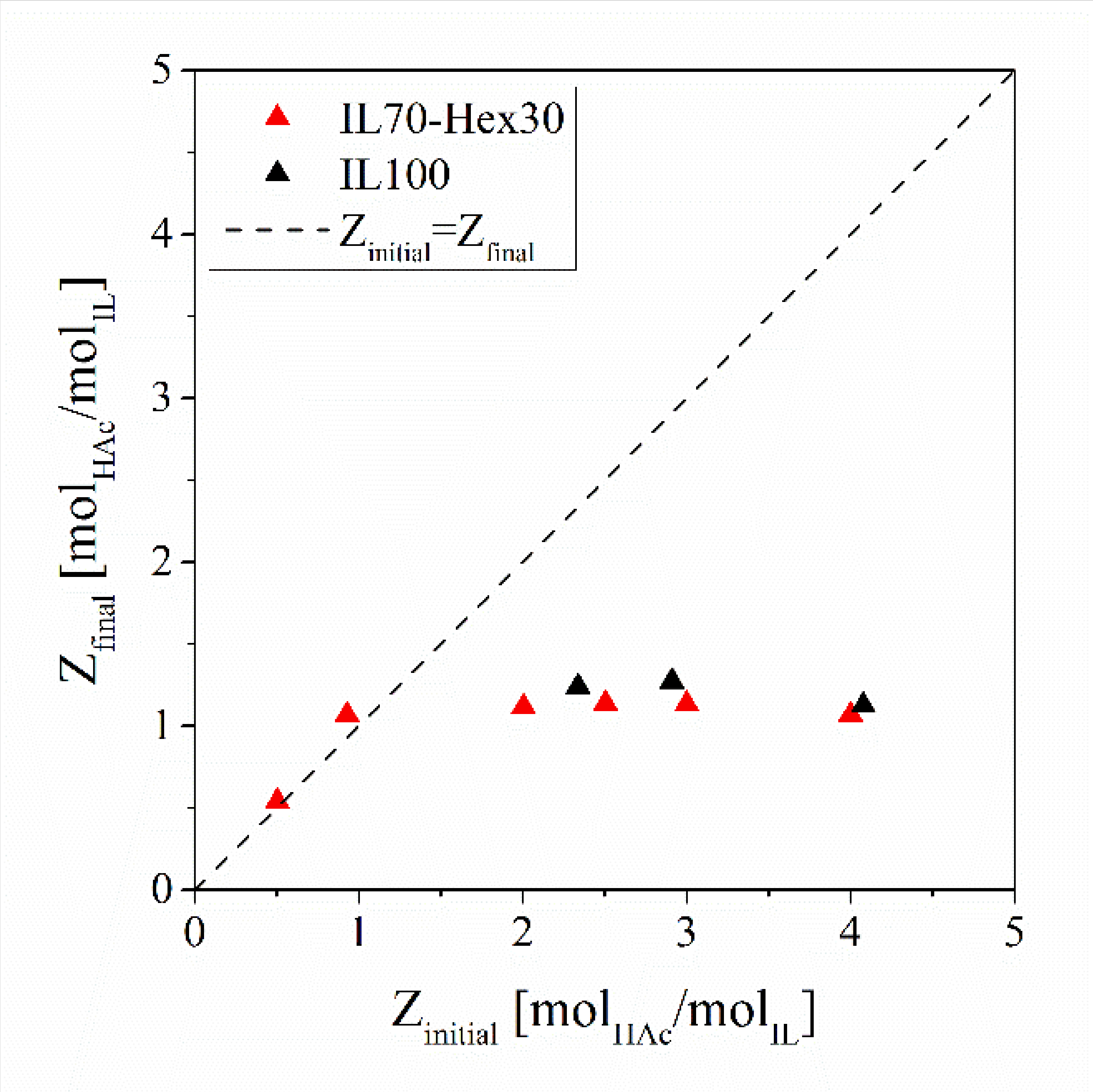




Schuur et al, Sep Purif Technol 2016 161 61-68

COMPARE WITH TRADITIONAL TOA
Improved D & S



Schuur et al, Green Chem 2019 21 2023

2 APPROACHES:

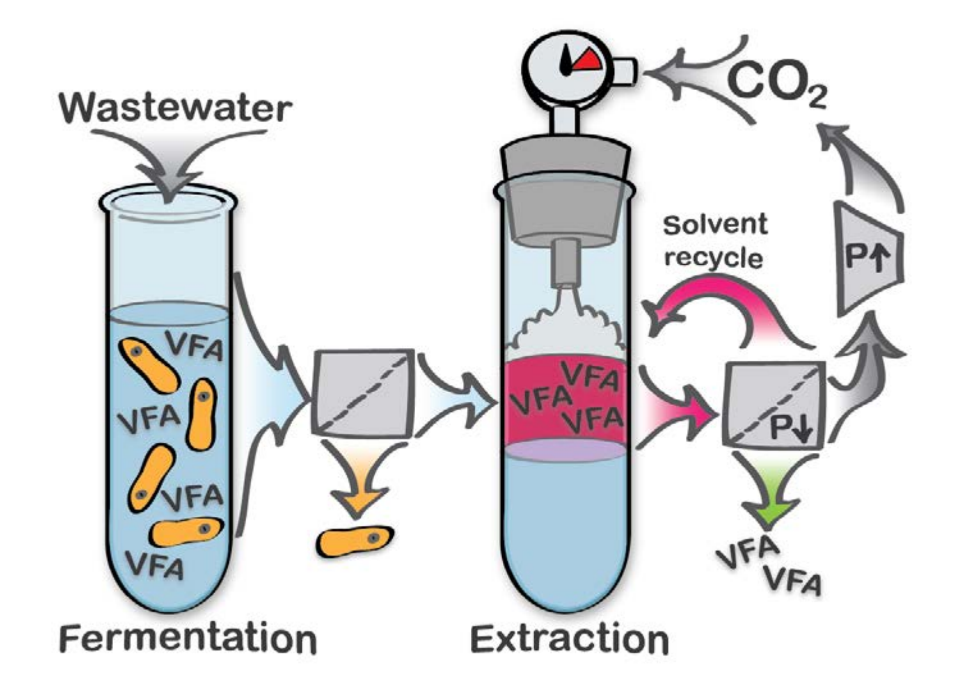
1) Get into the “higher concentration regime”

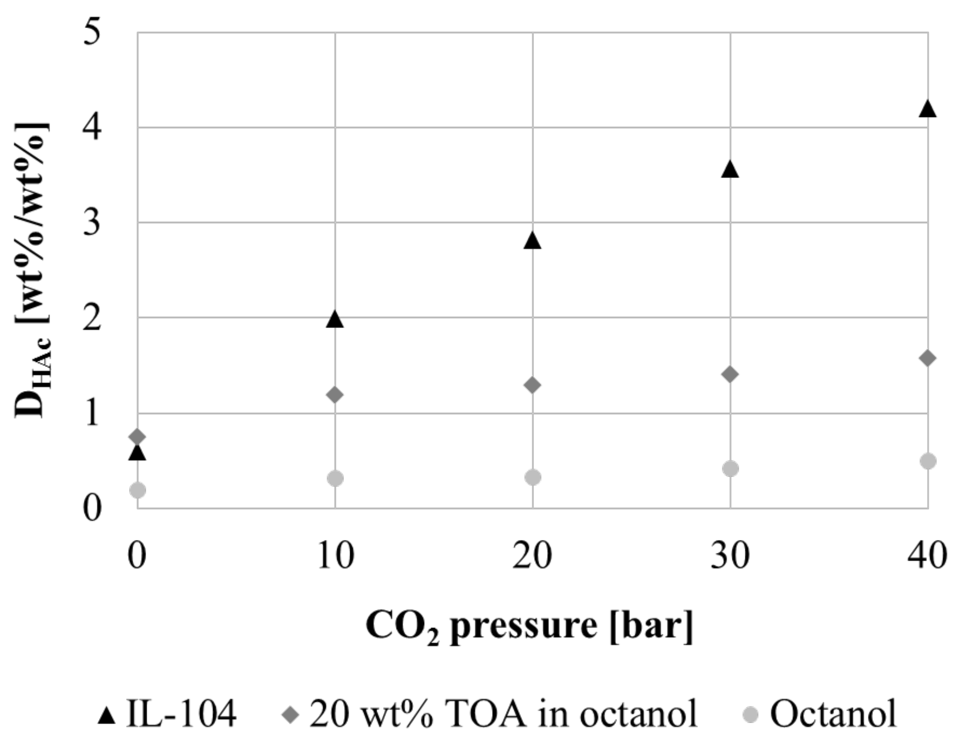
2) Reactive regeneration

DEEP REGENERATION CUMBERSOME

Highest affinity not necessarily good

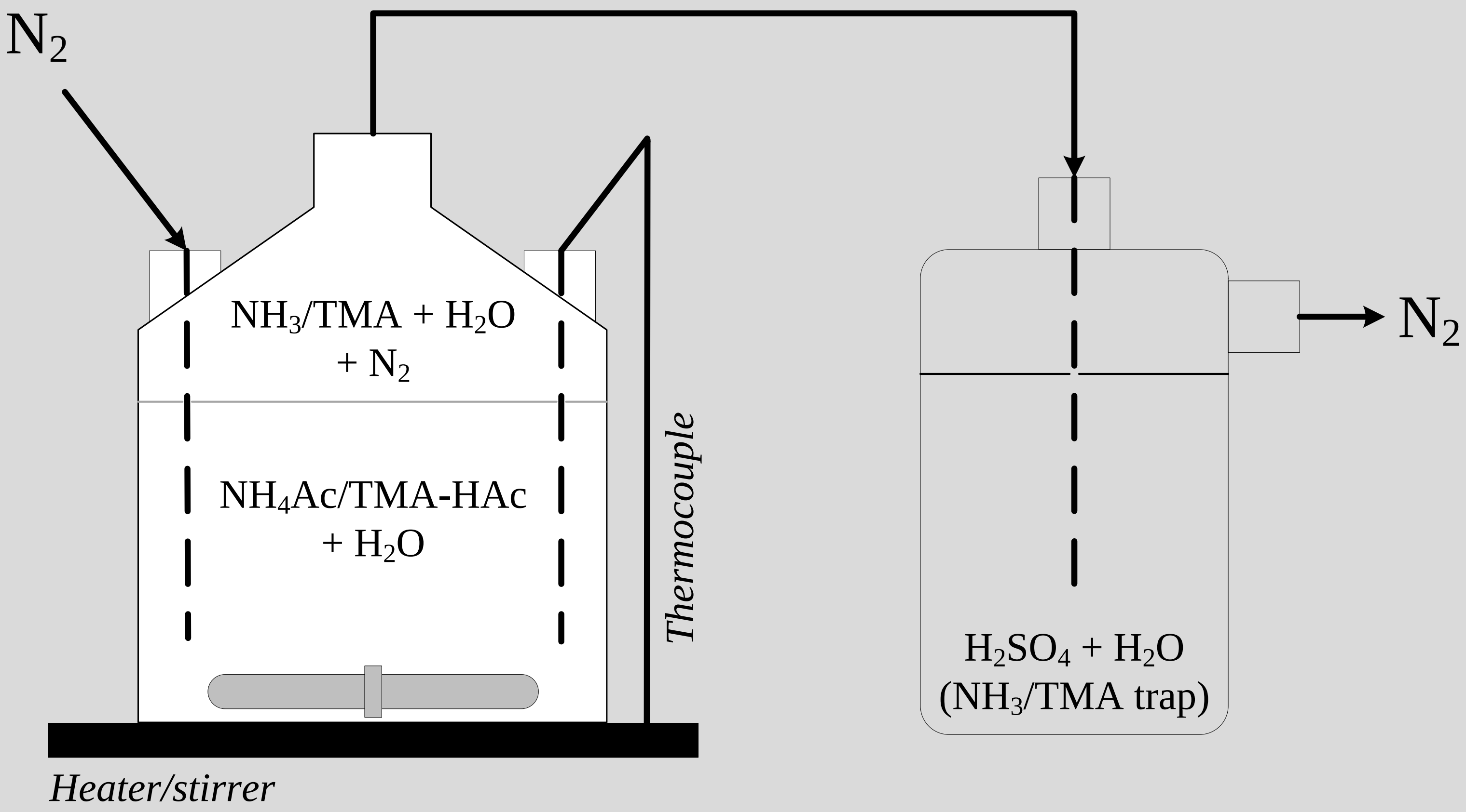
PRESSURIZED CO_2 & VOLATILE BASES
Improving extraction & enable regeneration





7 times higher D_{HAc} at 40 bar

Schuur et al, Green Chem 2015 17 4393-4400



END GOOD, ALL GOOD?

Schuur et al, Green Chem 2019 21 2023

→ Clear learning moment: high affinity can give difficulty

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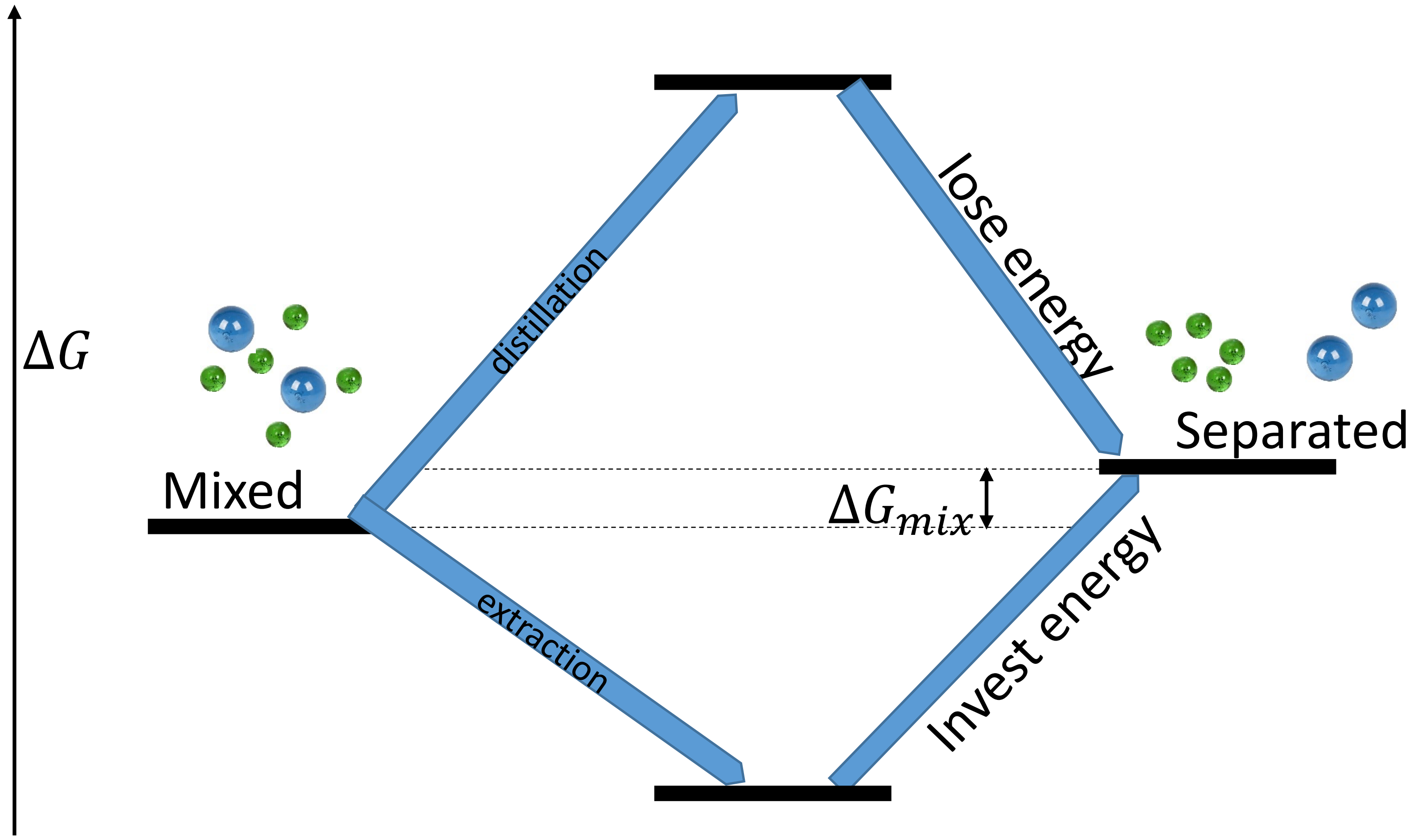

$$W_{sep} = -\Delta G_{mix} = RT\left(\sum_{i=1}^{N} x_i ln x_i + \sum_{i=1}^{N} x_i ln\gamma_i\right)$$

AFFINITY IN FLUID SEPARATIONS
IS THERE AN OPTIMUM AFFINITY?

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Performing an ITC assay

= a titration with heat measurement

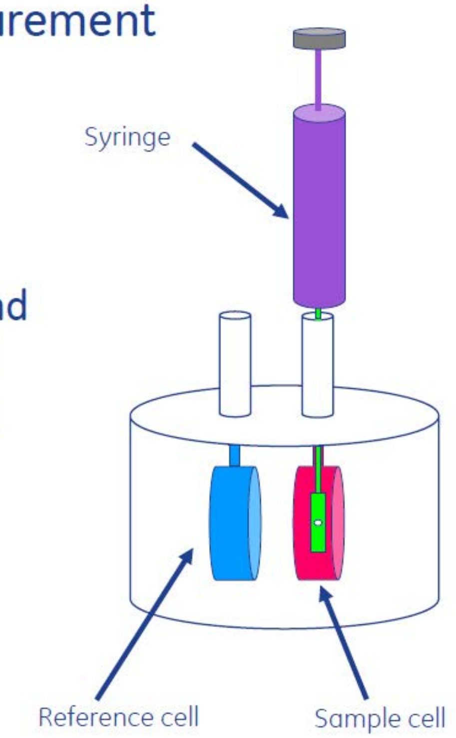
Binding partners:

- "Ligand" in syringe
- "Macromolecule" in sample cell

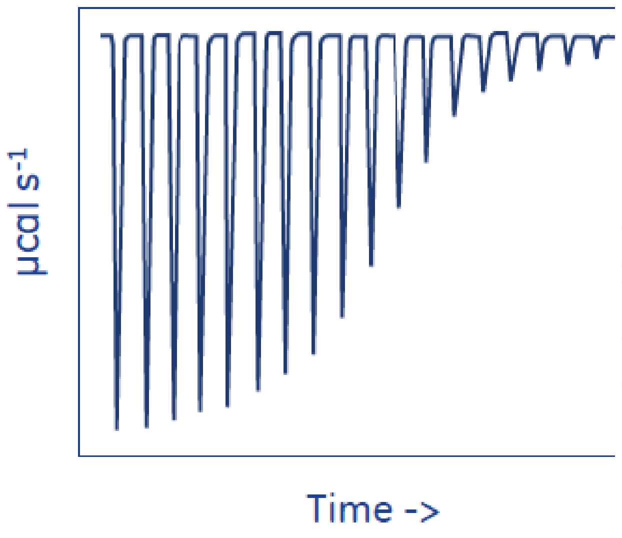
Heat of interaction between ligand and macromolecule is measured

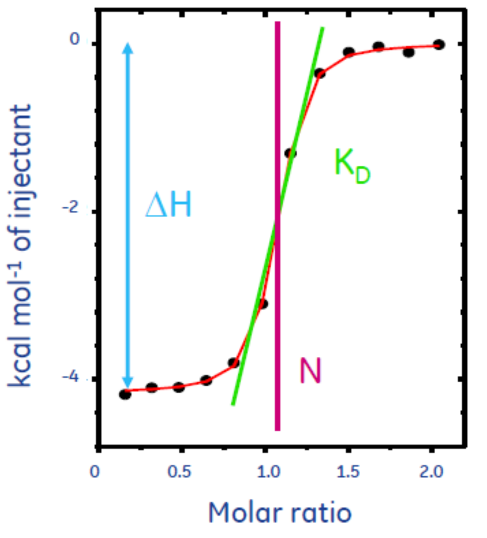
Parameters resolved from an ITC experiment:

- Affinity
- Binding Heat
- Number of binding sites
- Thermodynamics

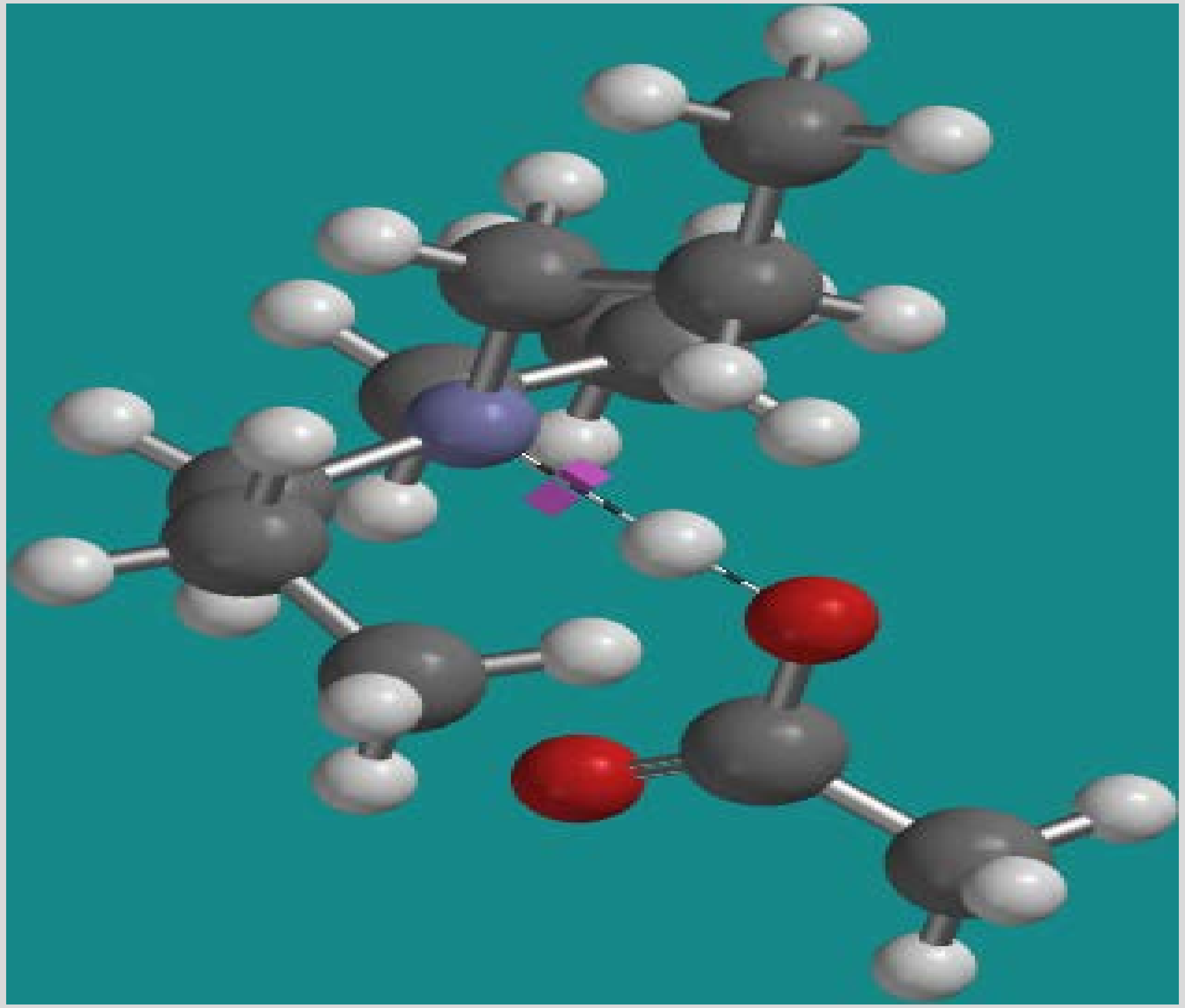


imagination at work





SPARTAN software for MM, here Hartree Fock



TPA – HAc

Study effect diluent

APPROACH: MEASURE & CALCULATE
ITC AND MOLECULAR MODELING

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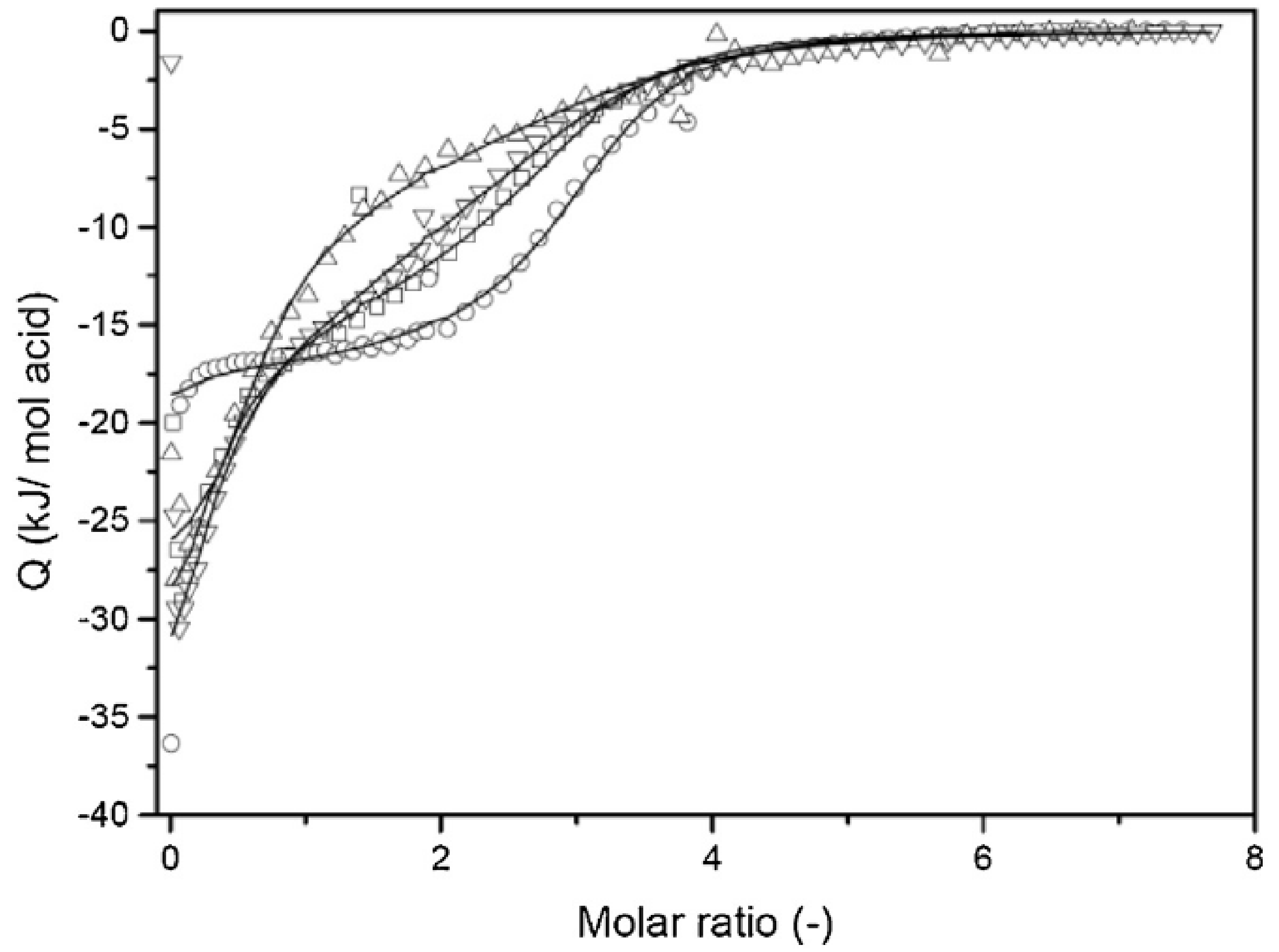
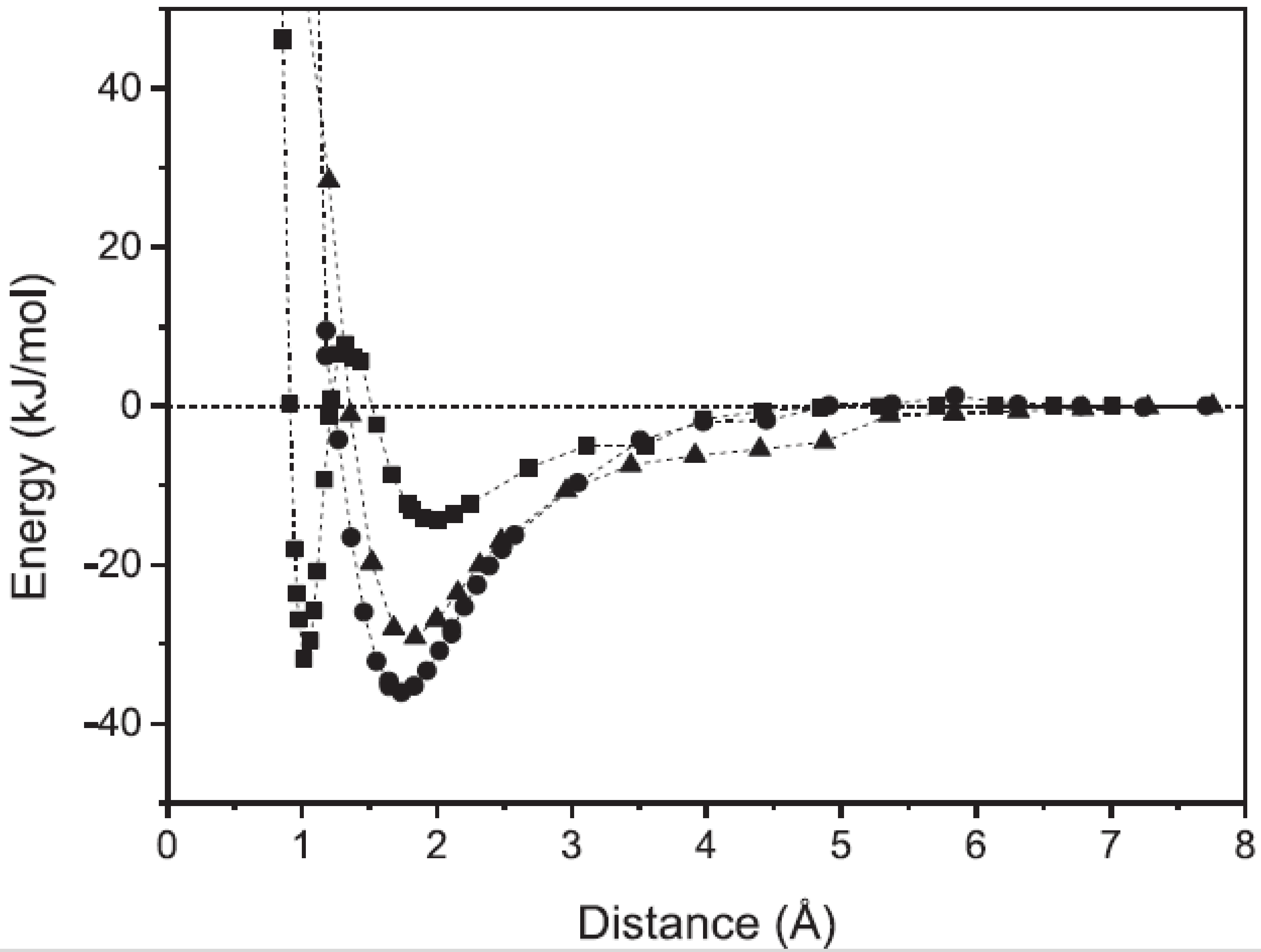


Fig. 7. Effect of 1-octanol concentration in the binary diluent of 1-octanol and toluene on the ITC 'S-curve' for the heat of complexation of the reaction of acetic acid with 1 M TOA (≈45 vol%) at 20 °C in: ○ 0% 1-octanol □ 50 vol% 1-octanol ▽ 75 vol% 1-octanol and △ 100 vol% octanol. Lines are fitted data with model parameters of Table 4.

J Ind Eng Chem 2019 72 364 (Sprakel & Schuur)



MM result Hartree Fock 6-31G*, SM8 for various diluents
J Ind Eng Chem 2019 72 364 (Sprakel & Schuur)

Also solvent design possible: J Mol Liq 2019 283 312

ITC and MM
Measurement & Interpretation

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Solvent selection/design important for biomass fractionation

Aromatics regeneration from IL works perfect

Difficult regeneration of acids from $P_{666,14}$ Phos

Balance Affinity!

or… stimuli responsive solvents?

CONCLUSIONS
Balancing Affinity Essential

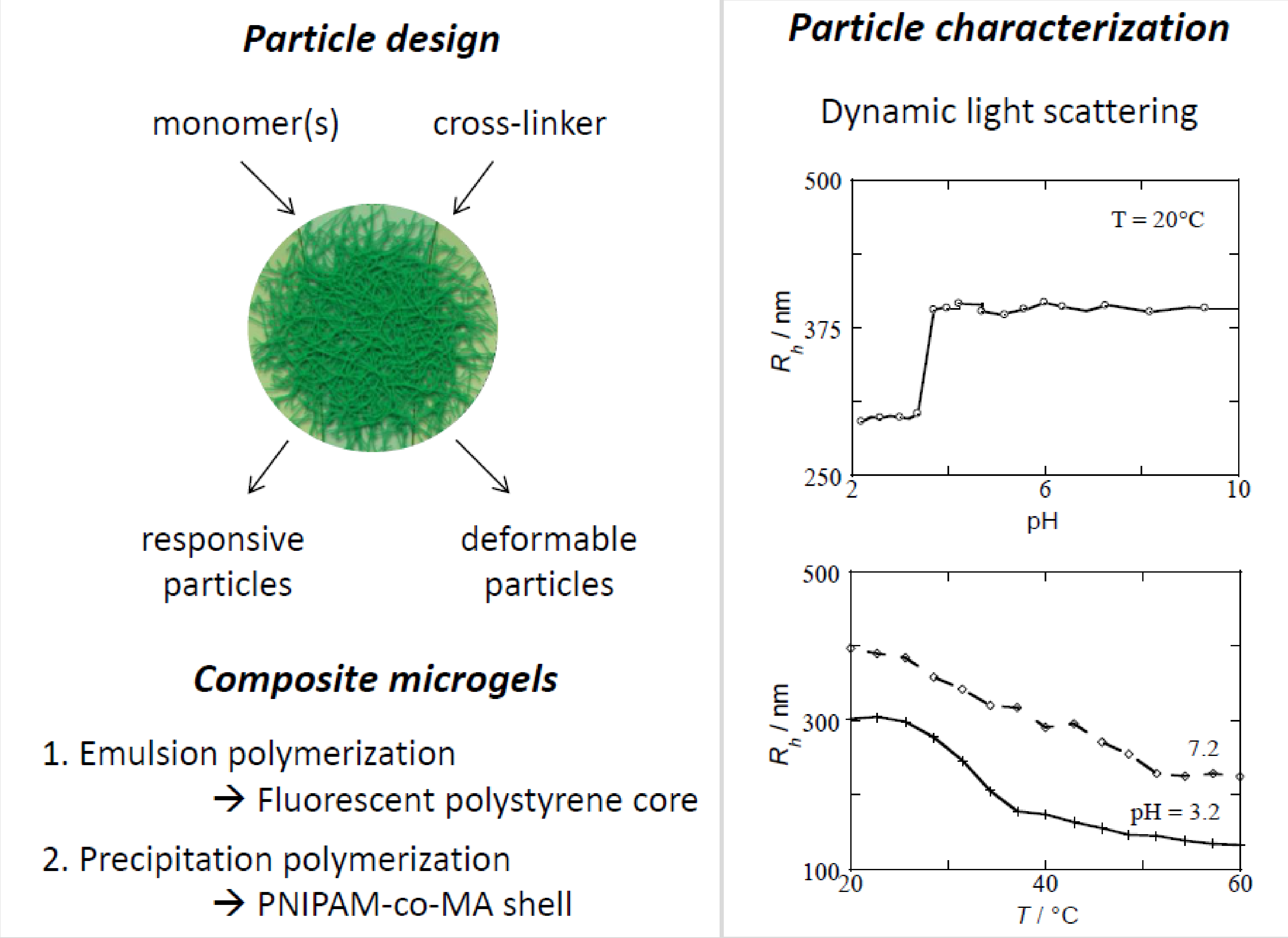
T-responsive

pH-responsive

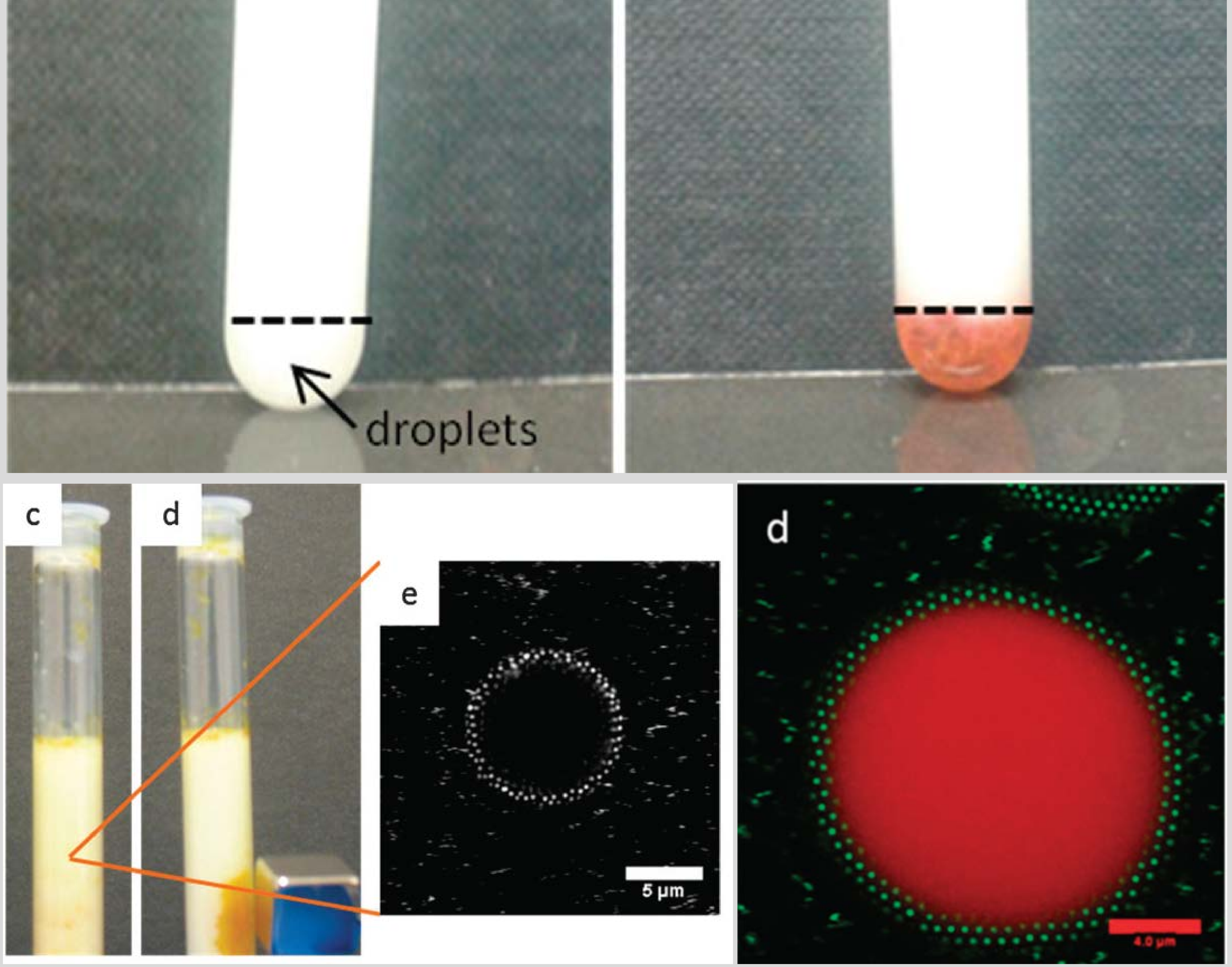
Photoresponsive

CO_2-response

STIMULI RESPONSIVE SEPARATIONS
Trying to keep conditions mild



Monteillet, 2015



1) **Emulsion breaking on command**
2) **Extraction of pigment, keeping protein functionality**

Sprakel et al, Chem Comm 2015 50 12197
Eppink et al, React Chem Eng 2018 3 182

CORE-SHELL STABILIZED IL EMULSIONS
Multiresponsive particles

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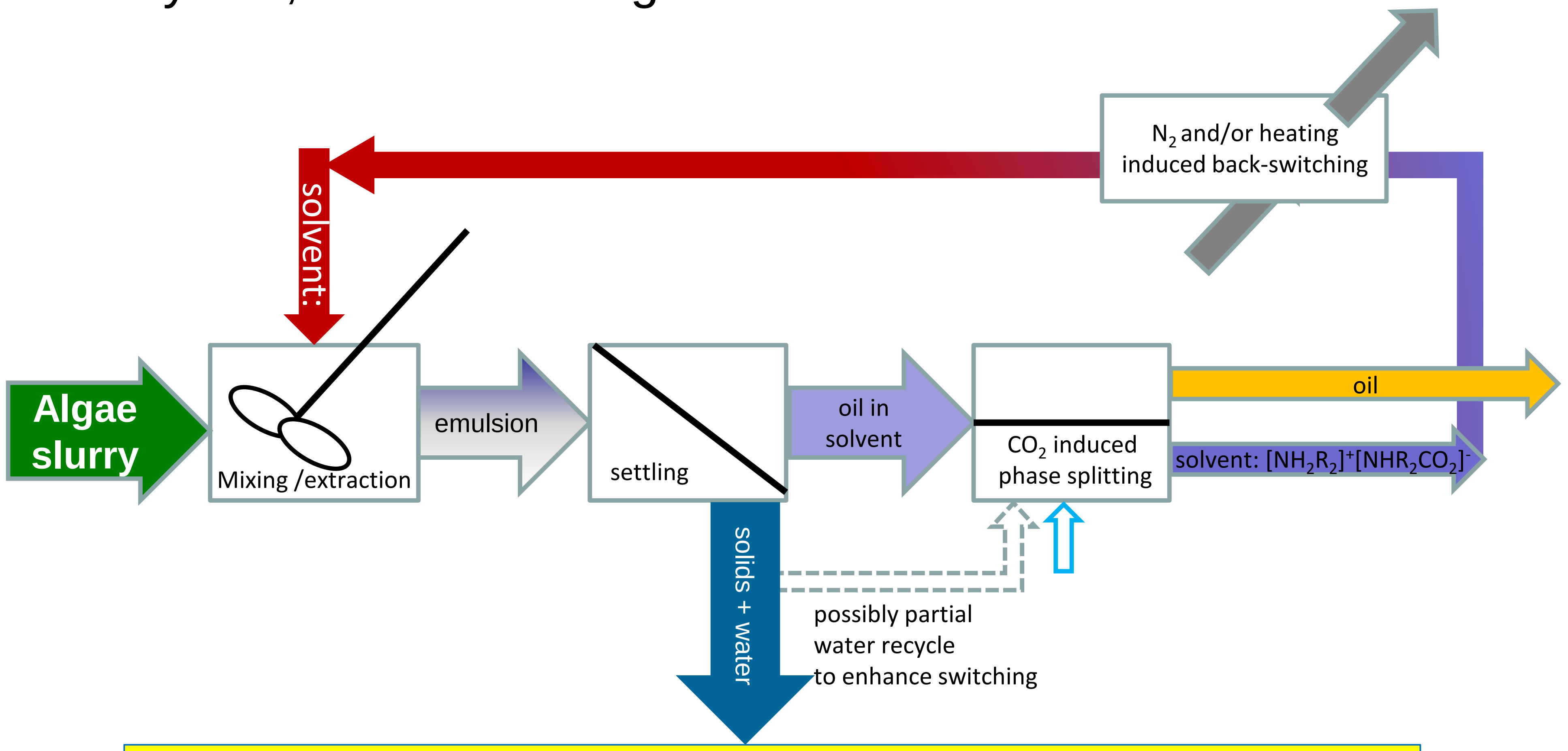
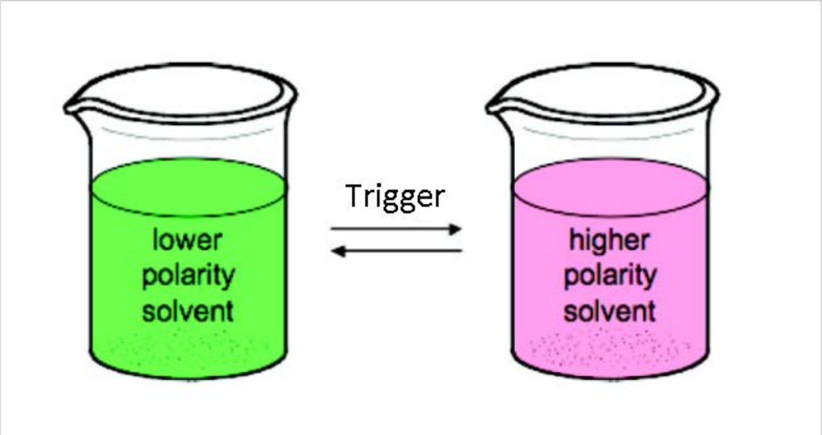
LIPID EXTRACTION FROM MICROALGAE
Switchable solvents

Preferably wet, non-broken algae



Ideal Solvent: good lipid extraction & easily switchable + back-switchable



Jessop et al., Nature 2005 436 1102

$$2\ R_2NH \underset{-CO_2}{\overset{CO_2}{\rightleftharpoons}} R_2NH_2^+ + R_2NCO_2^-$$

Biores Technol 2013 149 253
Algal Res 2015 11 271
Green Energ Environ 2016 1 79
Ind Eng Chem Res 2017 56 8073

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https://www.elsevier.com/events/conferences/international-conference-on-ionic-liquids-in-separation-and-purification-technology/submit-abstract

ILSEPT-4
Poster abstract submission still open

ISPT

Provides

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ACKNOWLEDGEMENTS

Thank you for your attention