Lignins and more

Biorefinery at the Institute of Chemical Engineering and Environmental Technology - TUGraz

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Challenges and solutions

Standard unit operations need to be adapted respectively new technologies need to be designed

- Challenges

  => dilute process streams

  => difficult process matrix (pH, T, suspended matter, cell debris, intra cellular products,….)

  => emulsion and crud formation

- Solutions

  => new technologies are partially there

  => membrane technologies are emerging

  => bioprocess technology in combination with chemical engineering early in the development

The working group

Started WS 2017

- New master program „Biorefinery Engineering" accompanied with built up of new working group

AG Biorefinery

- Isolation of valubales from process streams of the pulp and paper industry
  - Kraft Lignin
  - Lignosulfonates
  - Carboxylic acids
- (in-situ) isolation of valuables from fermentation broth
  - Carboxylic acids
  - Biocat. products
  - …..

Running projects

Flippr² - COMET (2017 – 2021)

- Development of continuously operated Kraft lignin isolation and process integration thereof

KrAcid – bridge 1 (2018 – 2021)

- Isolation of carboxylic acids from Kraft pulping

BET – Horizon 2020 (2015 – 2019)

- Master programs, innovative learning formates, etc…

Membrane separations - IEA task Annex 17 (2017 – 2019)

Direct cooperation (2018 - …..)

- REACH- solvent replacement, isolation of lignosulfonates, …

Research guideline

- Selective in-situ isolation of valuables (e.g. lactic acid) from aqueous process streams

Mass transfer unit operations

1. Thermodynamic basics
2. Hydrodynamic basics
3. Technology development
4. Process

Inlet stream knwon

pH, T, p

$c_{valuables}$, c_{others}

Outlet stream targeted

pH, T, p

$c_{valuables}$ = as high as possible

c_{others} = 0

Research guideline – reactive extraction

- Variation in the organic phase: ration between tri-octylamine (TOA)/1-octanol/*n*-undecane
- Carboxylic acid and concentration thereof (0.1 – 1 mol/L)
- Temperature (25 – 45°C)
- Back-extraction ($NaHCO_3$, H_2O, HCl)
- Transfer to liquid membrane permeation
- Increase of selectivity: further reactive extractants (Cyanex, Aliquat, TBP)

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Thermodynamic basics - phase equilibria

Determination of *n* and K_{St} $\quad nLA_{aq} + TOA_{org} \leftrightarrow (TOA(LA)_n)_{org}$

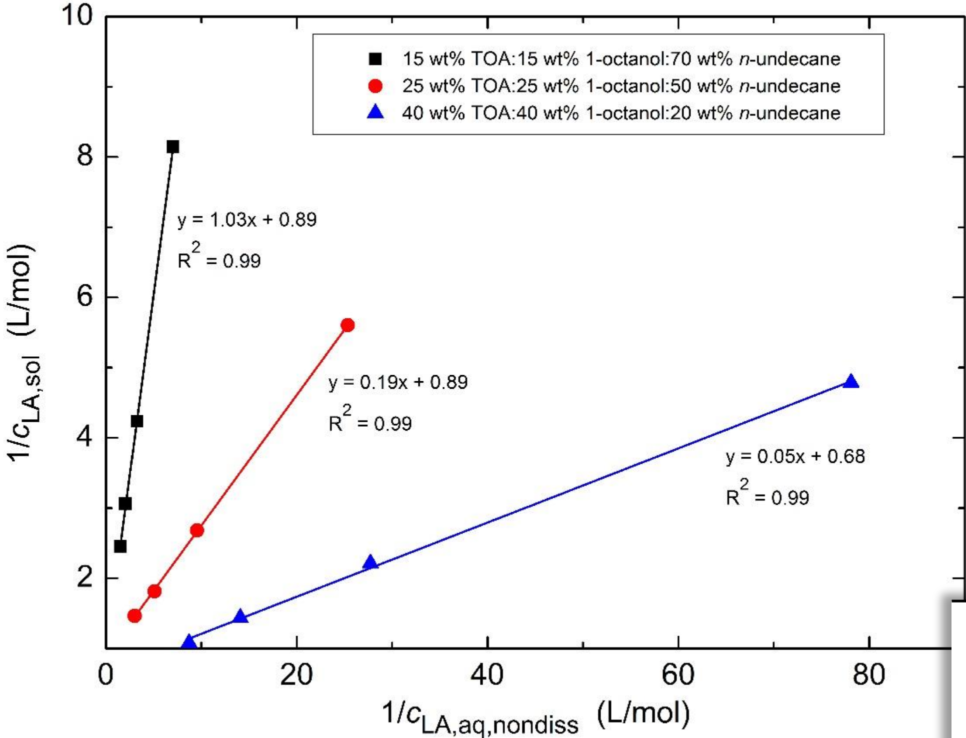
$$K_{st} = \frac{c_{TOA(LA)_{n},org}}{c^{n}_{HA,aq} \cdot c_{TOA,org}}$$

$$\frac{1}{c_{LA,\ org}} = \frac{1}{n \cdot K_{st} \cdot c^{n}_{LA,aq,nondiss} \cdot c_{TOA,0,org}} + \frac{1}{c_{TOA,0,org}} n$$

Determination of the selectivity

$$S_{a,b} = \frac{c_{b,stripp} \cdot c_{a,feed}}{c_{a,stripp} \cdot c_{b,feed}}$$

Results – lactic acid



TOA (wt%)	1-octanol (wt%)	n-undecane (wt%)	n	K_{St}
20	-	80	1.42	0.13
20	80	-	0.99	20.03
15	15	70	0.81	3.53
25	25	50	0.97	9.73
40	40	20	0.85	24.48

Results – carboxylic acid

- Concentration of the acids

The higher the concentration the higher is the extraction efficiency

- Lactic acid, acetic acid and formic acid

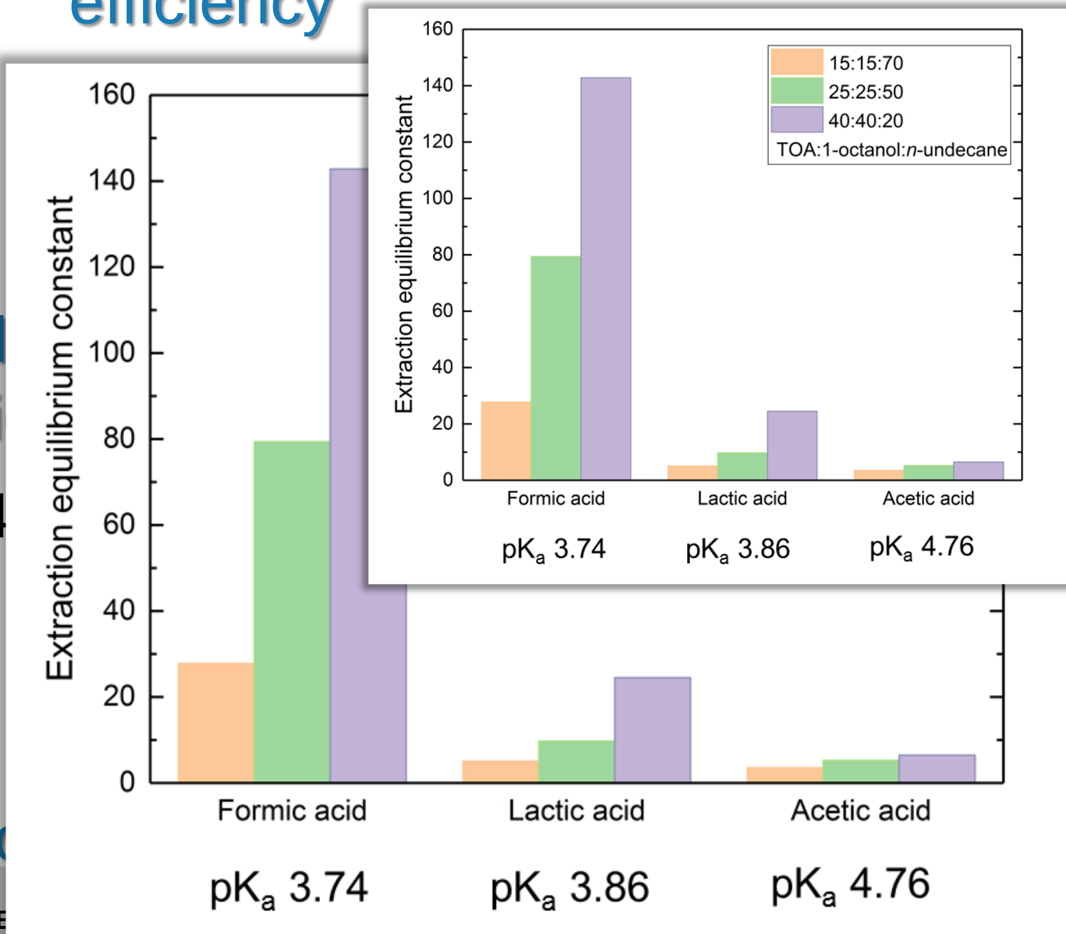
Extraction foll
pK_a of the aci

- Temperature (25 – 4

Temperature

- Stripping ($NaHCO_3$,

Back-extracti



Research question

- Selective in-situ isolation of valuables (e.g. lactic acid) from aqueous process streams

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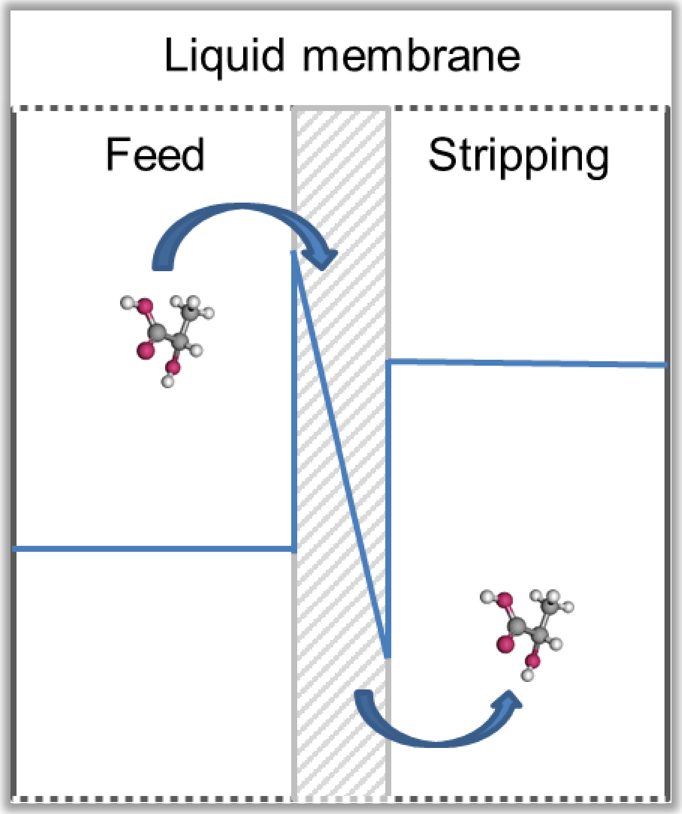
Results

- Transfer to liquid membrane permeation
- Selective separation



Results – liquid membrane permeation

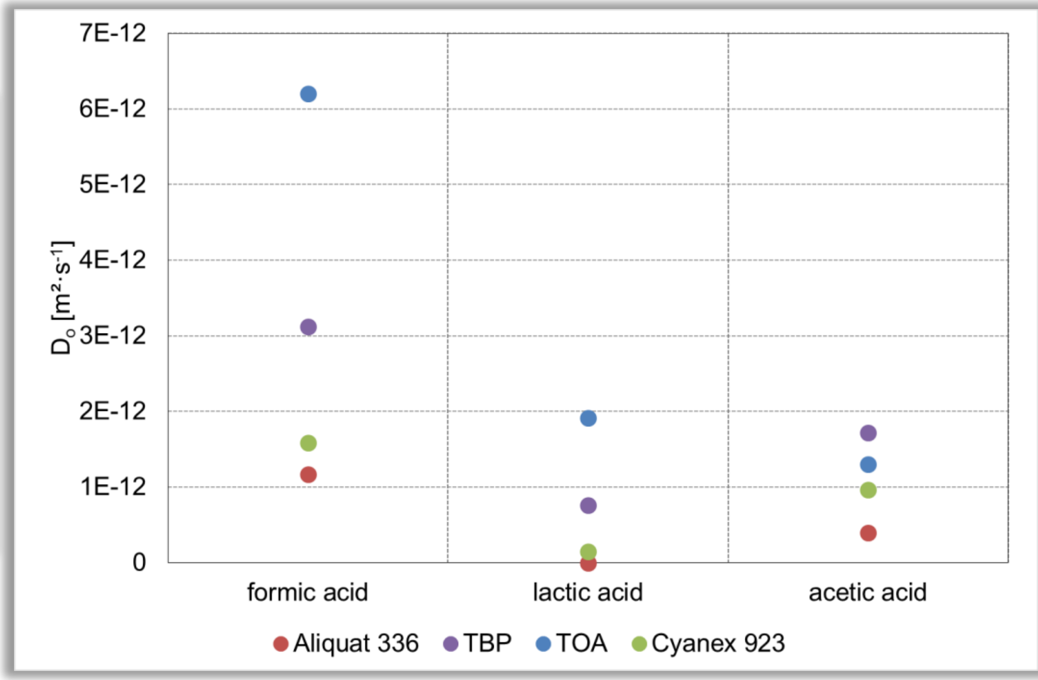
- Diffusion controlled mass transfer

$$j = \frac{V}{A \cdot \varepsilon} \cdot \frac{dc}{dt}$$

$$[c_0] - [c] = \frac{[TOA]_{tot}}{n \cdot \frac{d_0}{D_0}} \cdot \frac{A \cdot \varepsilon}{V} \cdot t$$

- Further reactive extractants/selectivity

Liquid membrane	FA/ LA	FA/ AA	AA/LA
TOA	2.04	2.57	0.79
Aliquat 336	∞	2.1	∞
TBP	2.67	1.26	2.12
Cyanex 923	8.5	1.16	7.32



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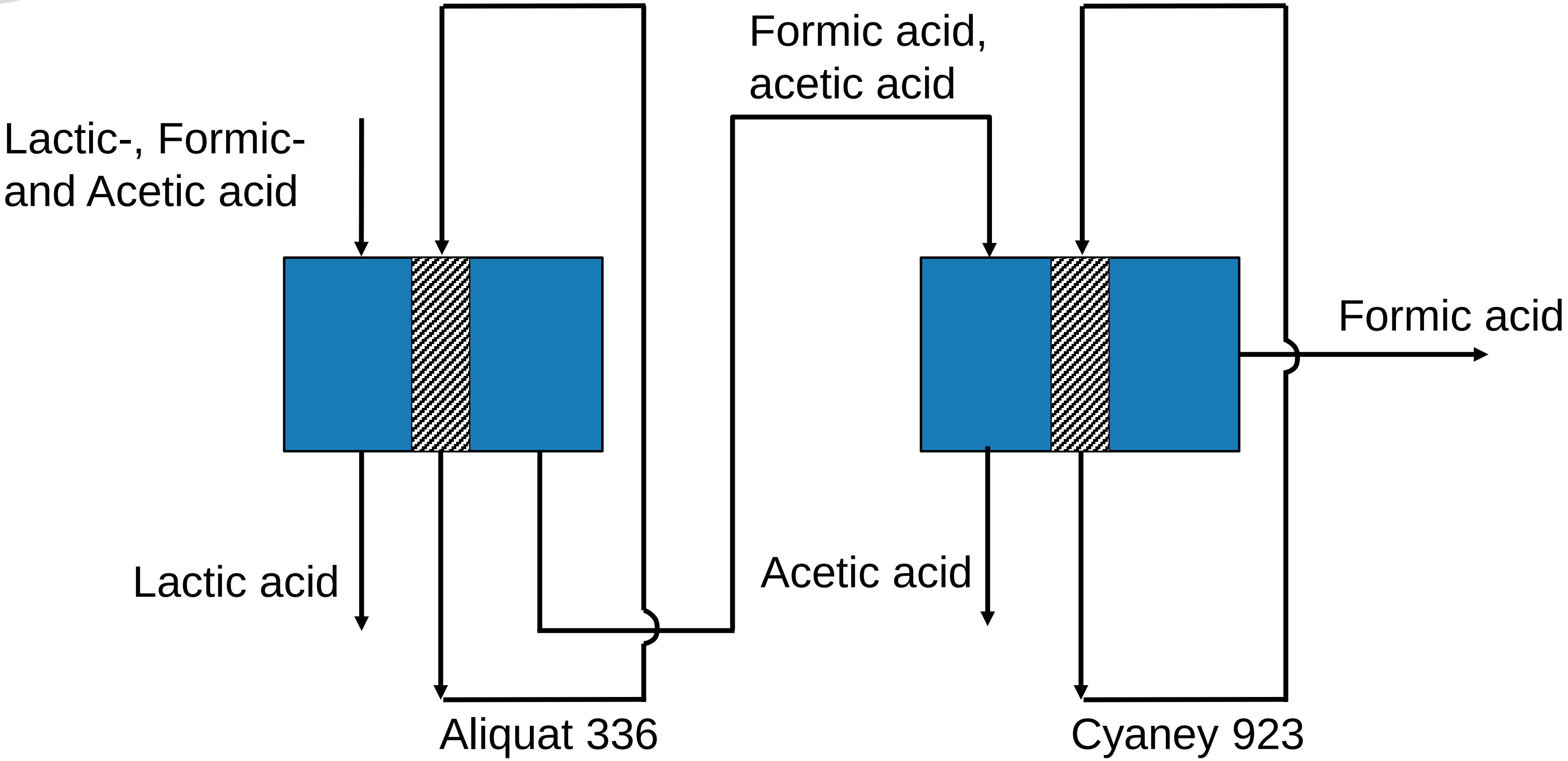
Process

- Selective in-situ isolation of valuables (e.g. lactic acid) from aqueous process streams



Conclusion

- The working group biorefinery engineering
- Isolation of valuables from process streams in the biobased environment – challenges and approach
- Carboxylic acid isolation from modeled fermentation broth
- Phase equilibria data
- Emulsion prevention
- Liquid membrane permeation as potential future technology
- Process optimization – two-step process

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Work

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You

For your attention

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