On coupling salt extraction from black liquor with hydrothermal liquefaction of its organic content

BL2F Final event - Online

07-03-2024

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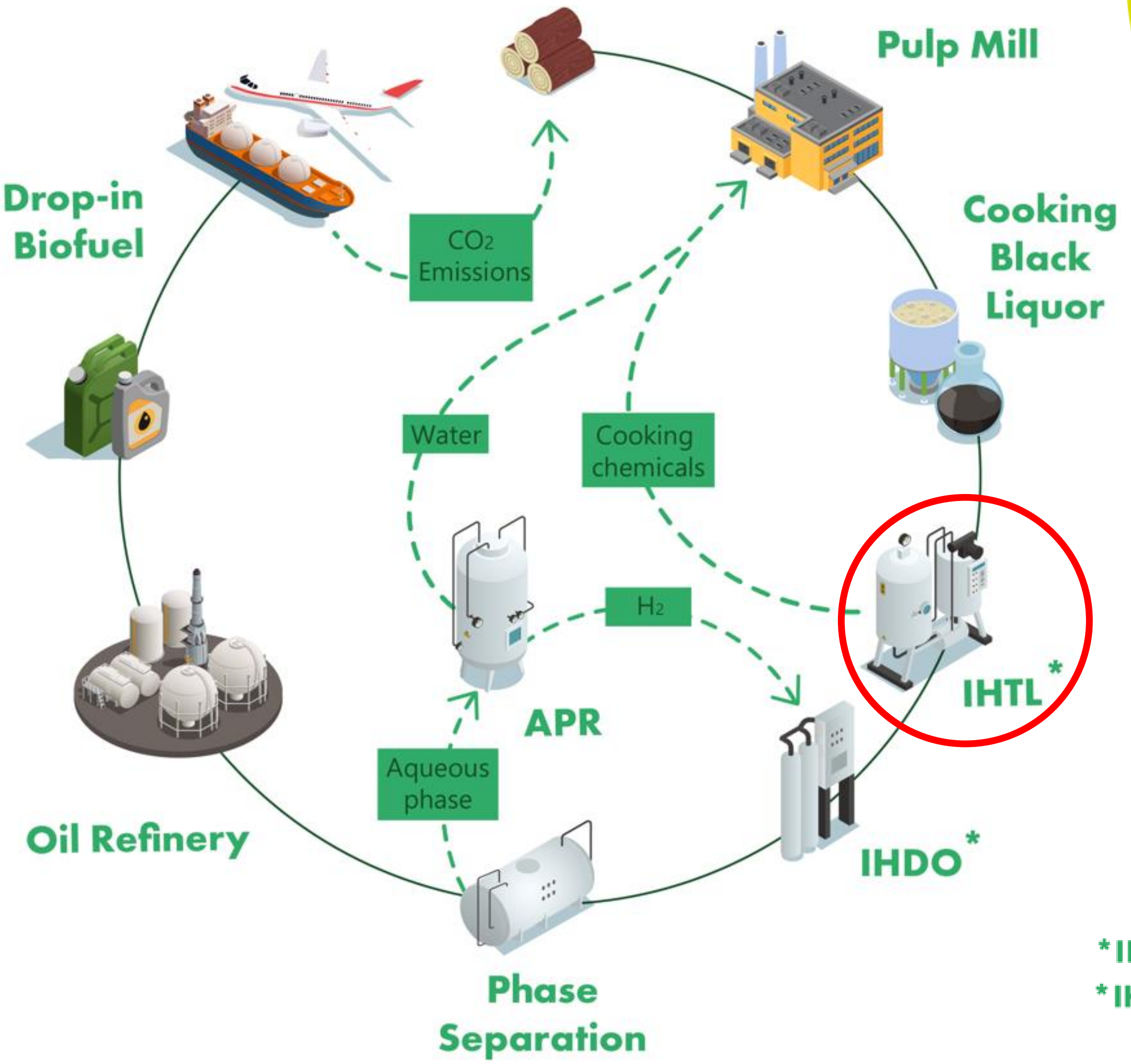
BL2F

Transforming Black Liquor to Biofuel

This project has received funding from the European Union Grant Number 884111

Extracting salts from BL during HTL step



*IHTL Integrated Hydrothermal Liquefaction
*IHDO Integrated Hydrodeoxygenation

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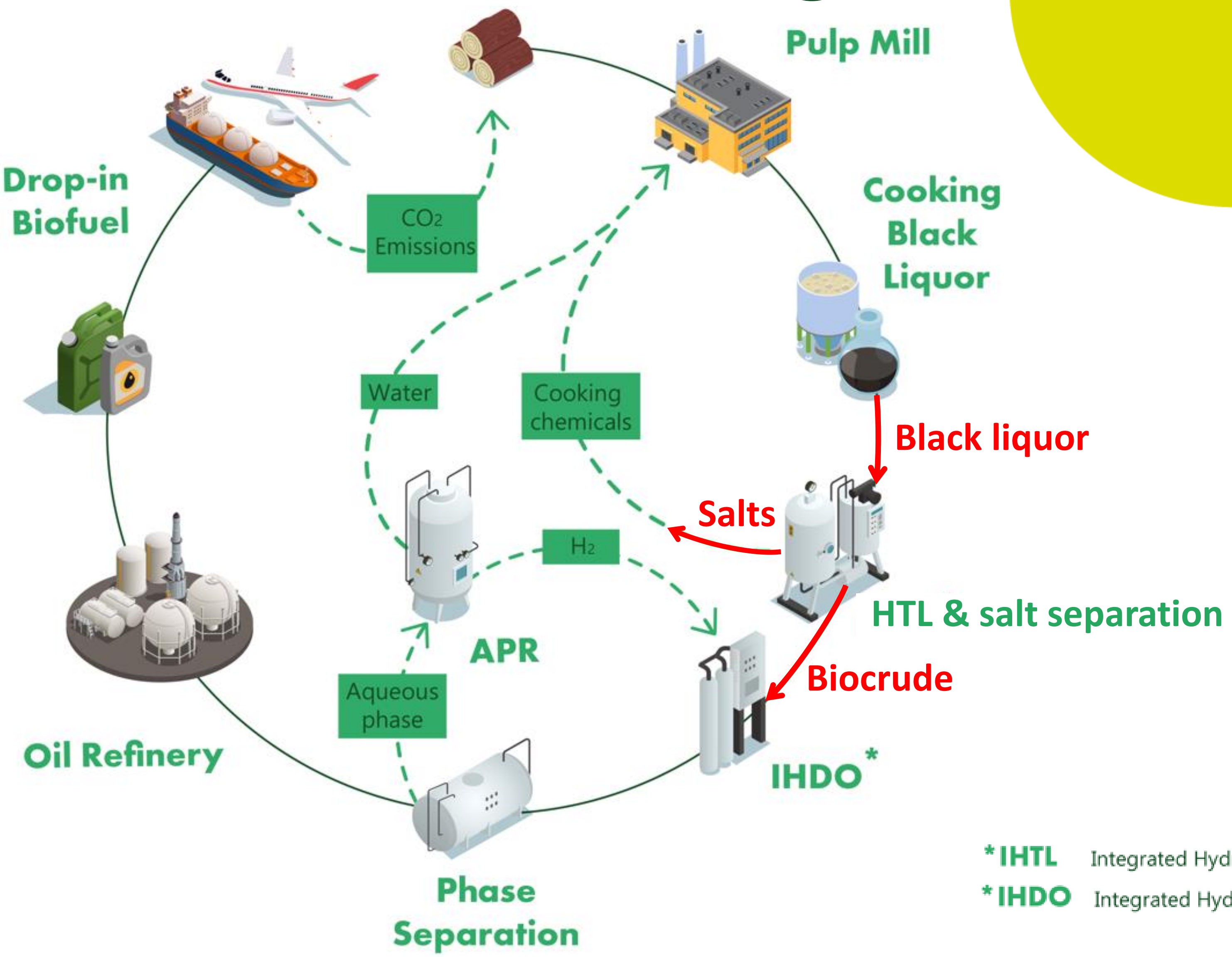
Extracting salts from BL during HTL step



*IHTL Integrated Hydrothermal Liquefaction
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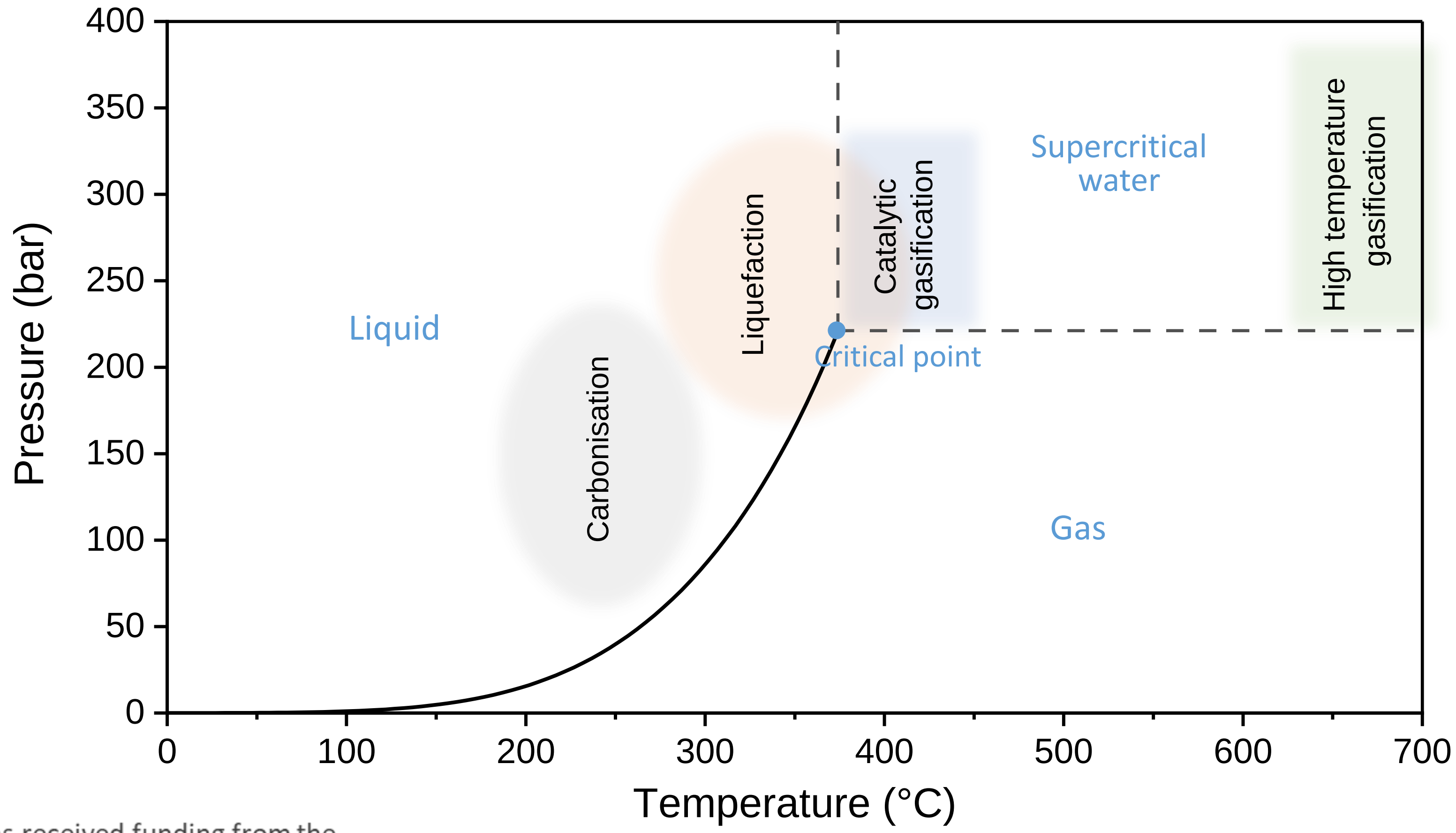
Hydrothermal valorization of wet biomass

- Broad variety of chemical energy carriers possible



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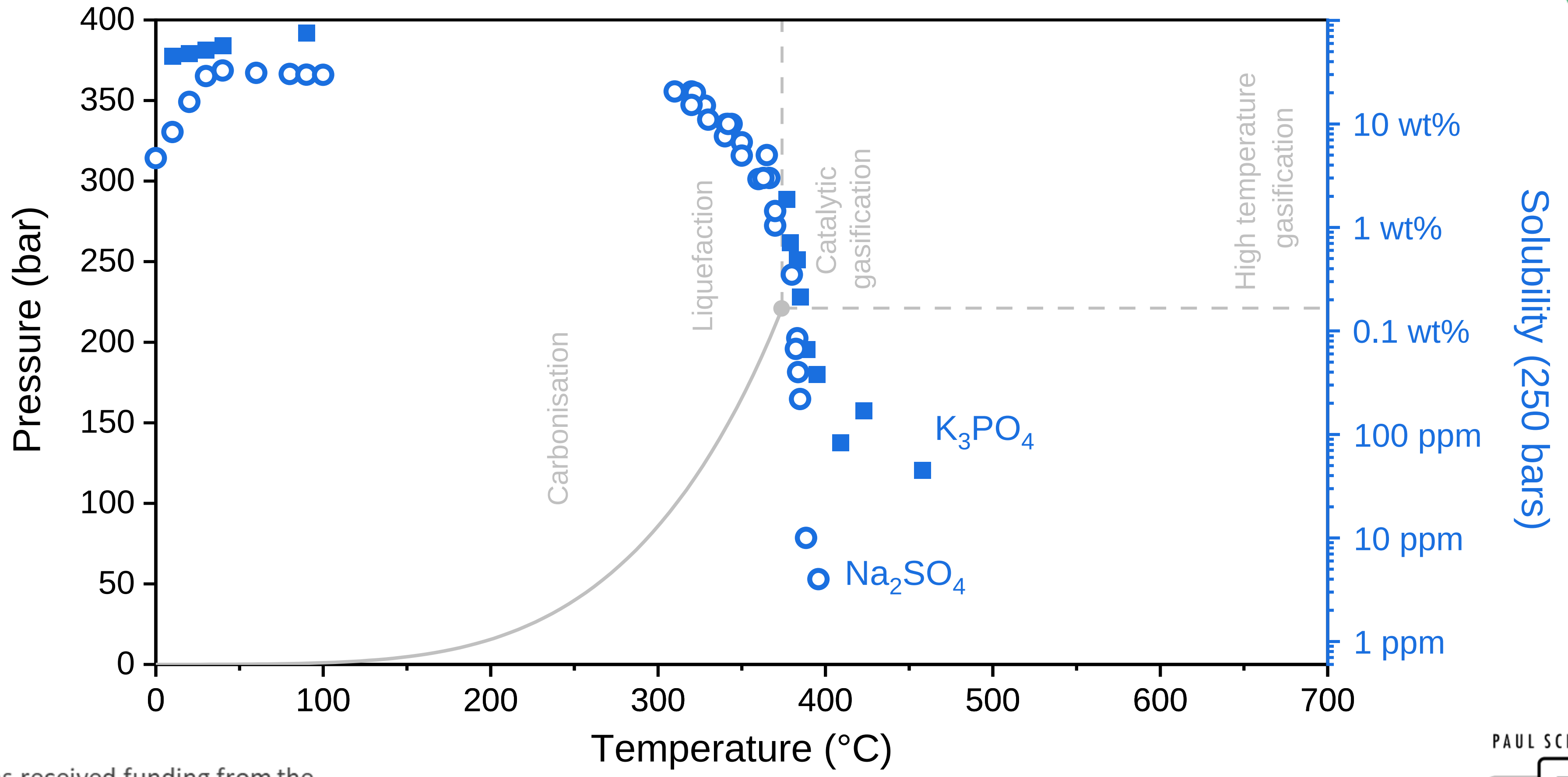
Hydrothermal valorization of wet biomass

- Solubility of salts drops drastically



This project has received funding from the

Ding et al., Fluid Phase Equilib. 483 (2019) 31 ; Lemoine et al., J. Supercrit. Fluids 130 (2017) 91

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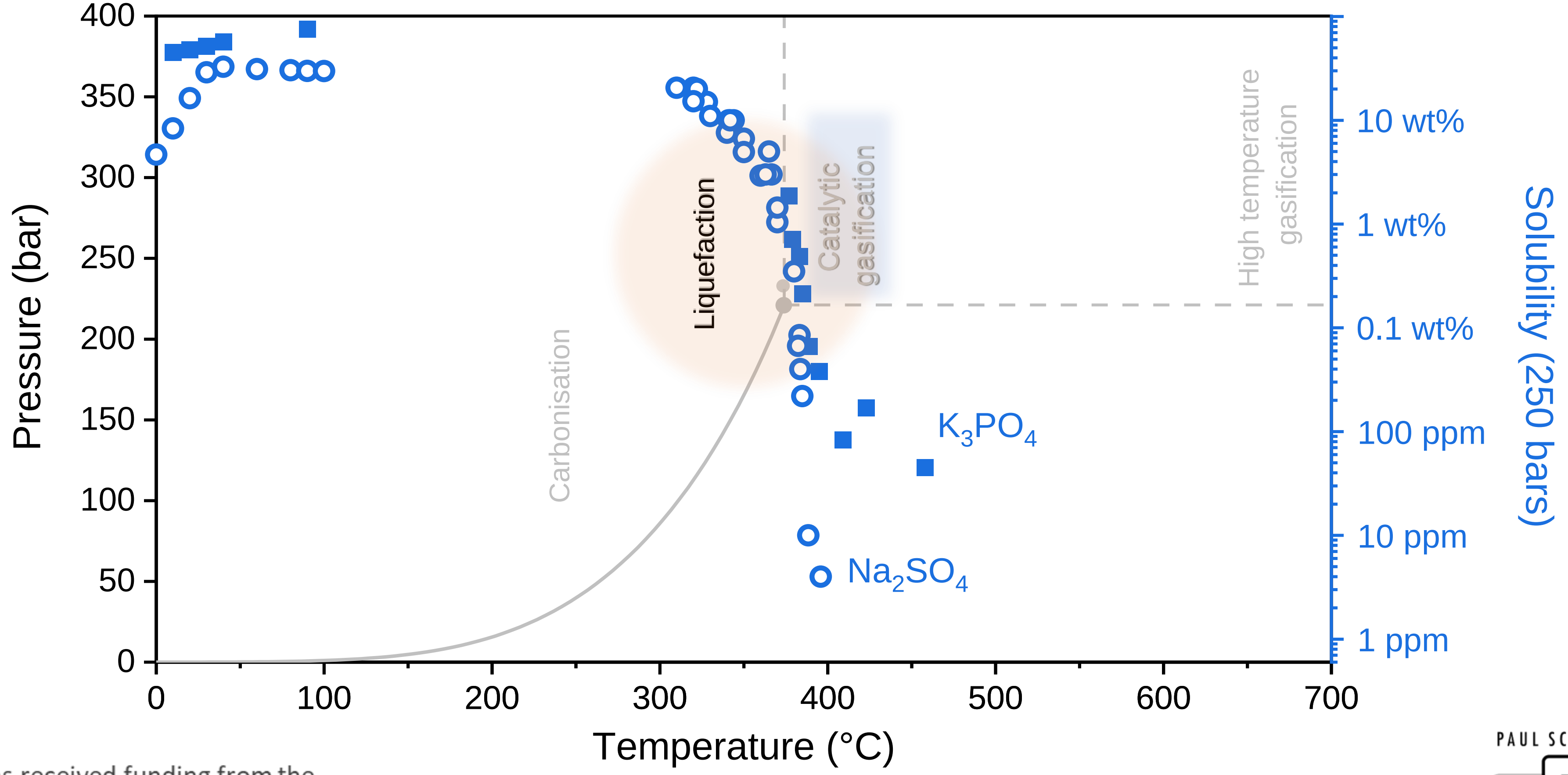
Hydrothermal valorization of wet biomass

- One can exploit low salt solubility for gasification and high temperature liquefaction



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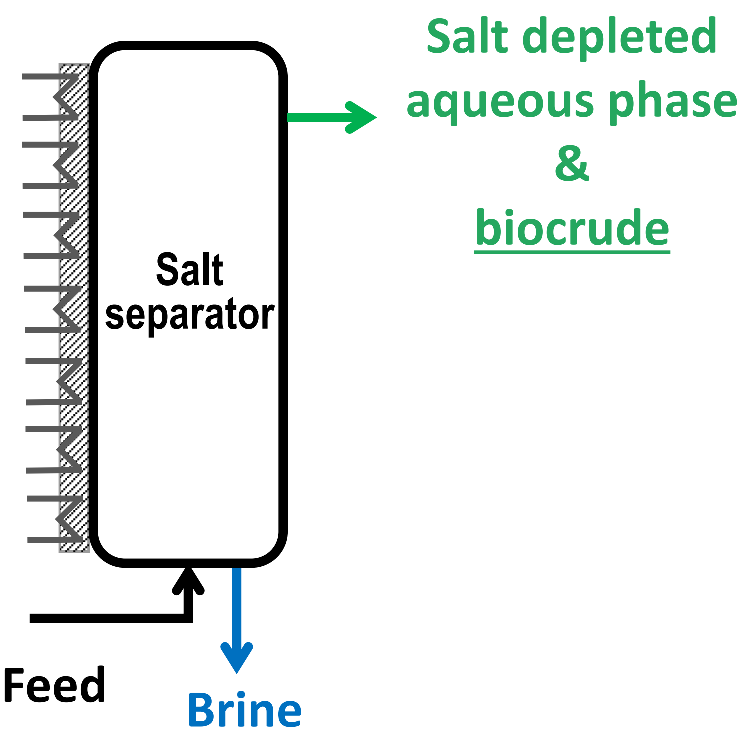
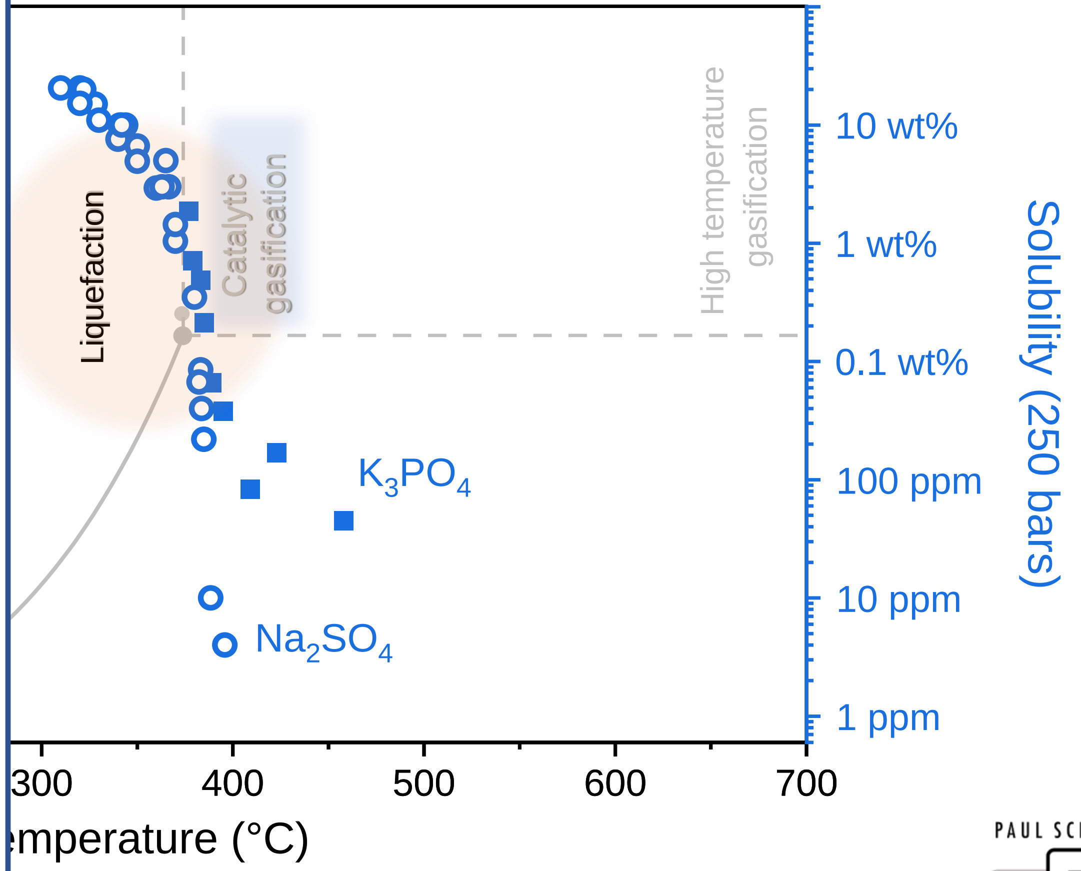
Objectives of WP2

- Identify a strategy to allow steady salt extraction
- Optimize salt extraction
- Optimize the coupling of salt extraction and HTL

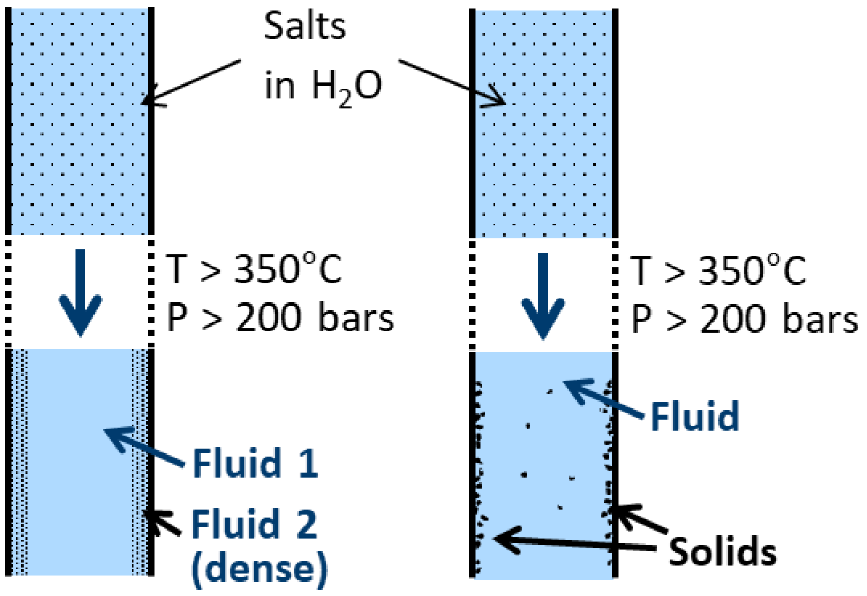




Ding et al., Fluid Phase Equilib. 483 (2019) 31 ; Lemoine et al., J. Supercrit. Fluids 130 (2017) 91

Salt phase behavior under Supercritical water: challenges

- Risk of clogging for type 2 salts
- Phase behavior of salt mixture cannot be predicted



Type 1 salts
(MOH, K_3PO_4, K_2CO_3); M=Na/K

Type 2 salts
(M_2SO_4, Na_2CO_3, Na_3PO_4); M=Na/K

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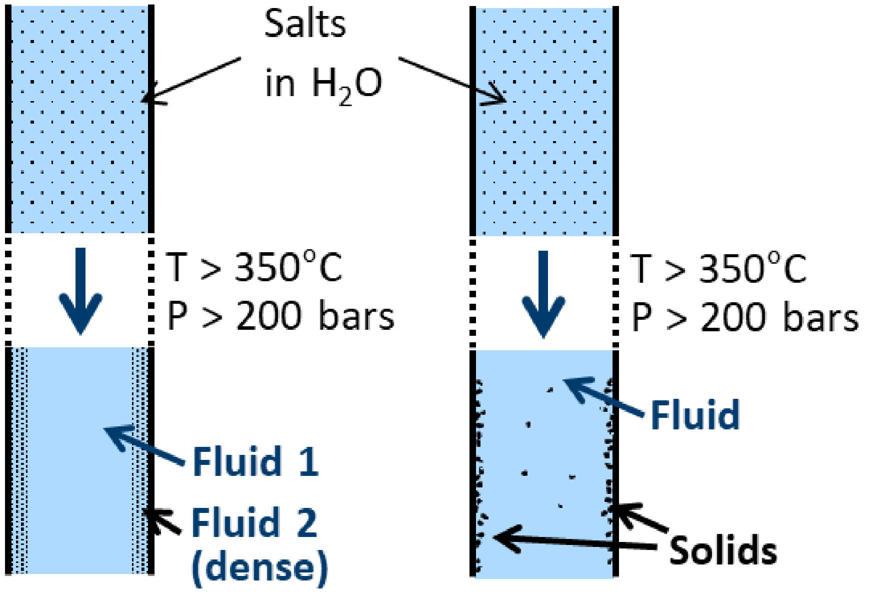
Salt phase behavior under Supercritical water: challenges

- Salts in model black liquor are type 2



Type 1 salts

(MOH, K_3PO_4, K_2CO_3); M=Na/K

Type 2 salts

(M_2SO_4, Na_2CO_3, Na_3PO_4); M=Na/K

Model Salt Solution from Characterisation – Reference Point

Salt	Type	wt.% in pristine BL	g/kg	mmol/kg
NaOH	1	1.74	17.4	435.0
NaHS	1	0.51	5.1	91.0
Na_2SO_4	2	0.40	4.0	28.4
Na_2CO_3	2	1.45	14.5	137.2
K_2CO_3	1	0.27	2.7	19.6
Total	**2**	4.4	43.8	711.1

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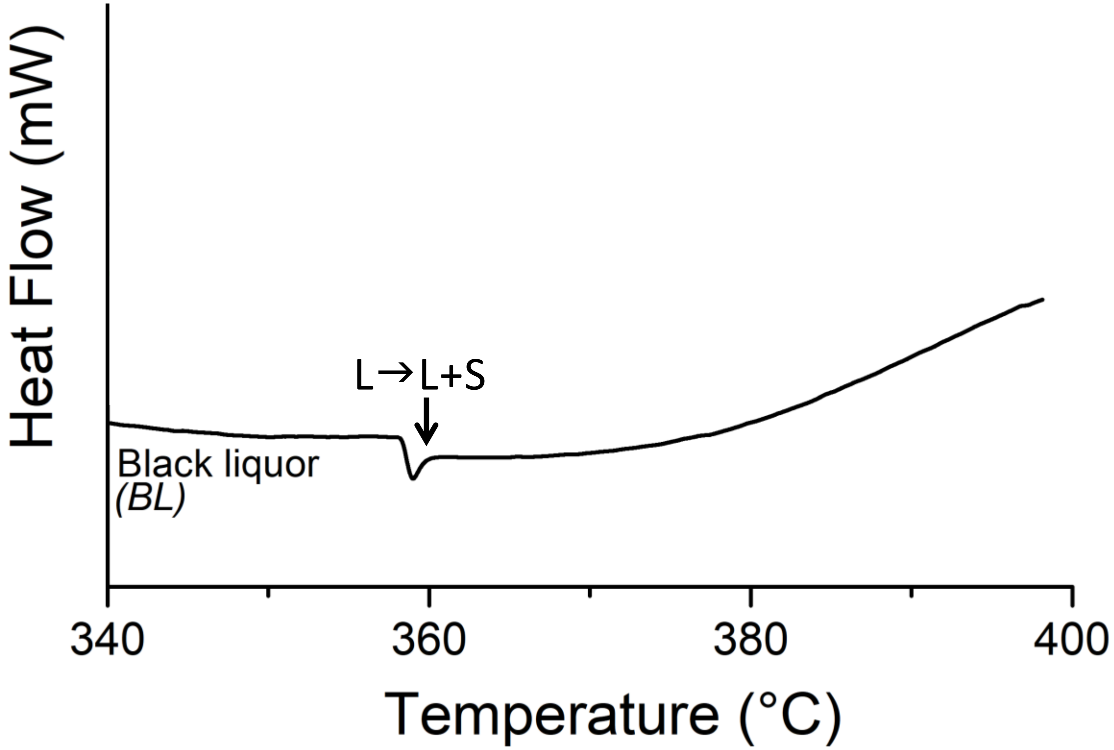
HP-DSC: salt phase behavior study

- With Black Liquor model salt solution, precipitation and fouling observed at 420°C & 250bars on continuous setup



In-house made Titanium Grade 5 crucibles

Canabarro N. I. et al, J. Supercrit. Fluids, accepted

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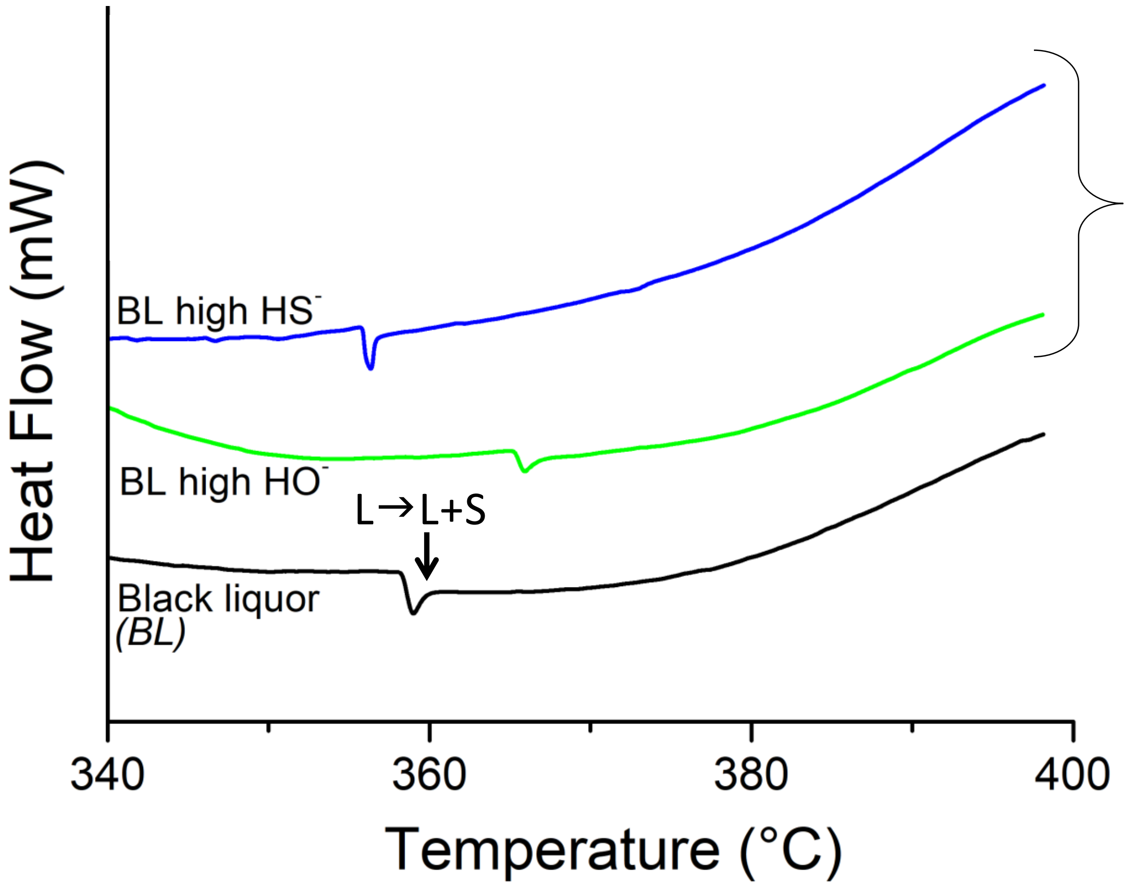
HP-DSC: salt phase behavior study

- Increase HS- and/or HO- ratio (type I) has limited impact on phase behavior



Strategy 1:
increase type 1 salt concentration (NaOH & NaSH)

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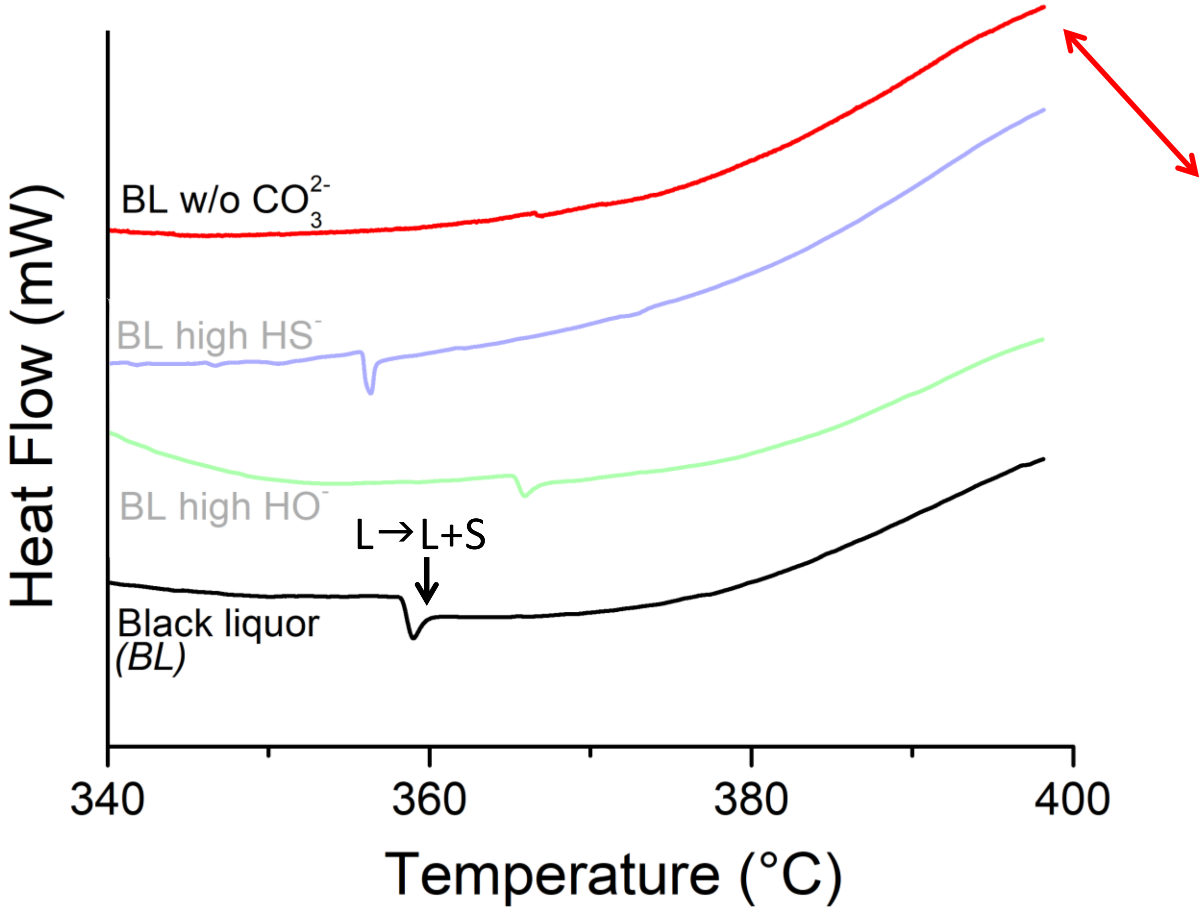
HP-DSC: salt phase behavior study

- Global type 1 behavior observed when feed is causticized



Strategy 2:

Causticization, e.g. with $Ca(OH)_2$:

$$Ca(OH)_{2(s)} + M_2CO_{3(aq)} \leftrightarrows 2\ MOH_{(aq)} + CaCO_{3(s)}$$

Type 2 *Type 1*

⇨ **Causticization is a promising strategy**

Canabarro N. I. et al, J. Supercrit. Fluids, accepted

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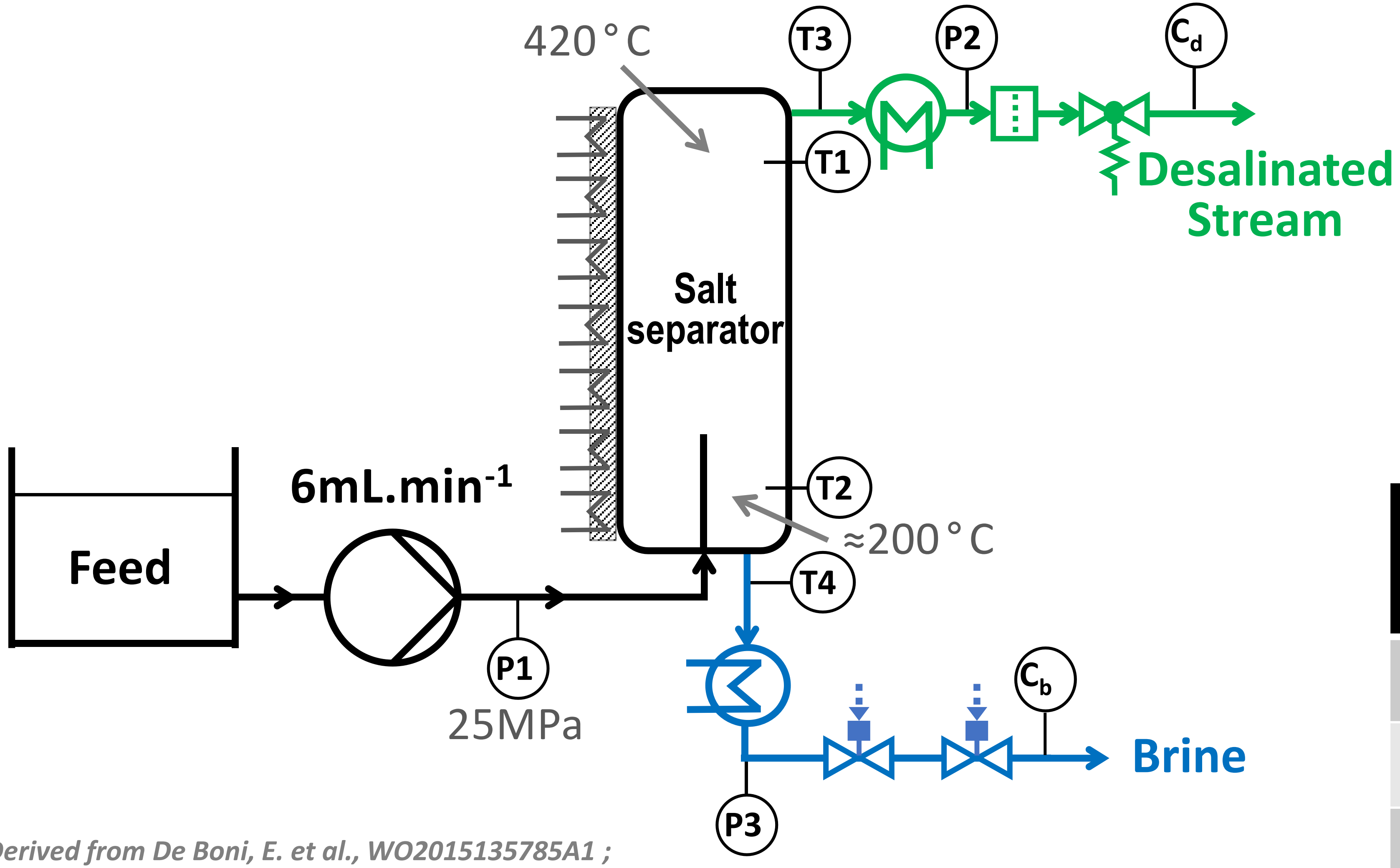
Continuous salt separation: test rig



Flow (mL.min^{-1})	Hydraulic residence time (min)
1	≈15
6.3	2.8
20	≈1

Derived from De Boni, E. et al., WO2015135785A1 ; Reimer et al., J. Supercrit. Fluid 117 (2016)

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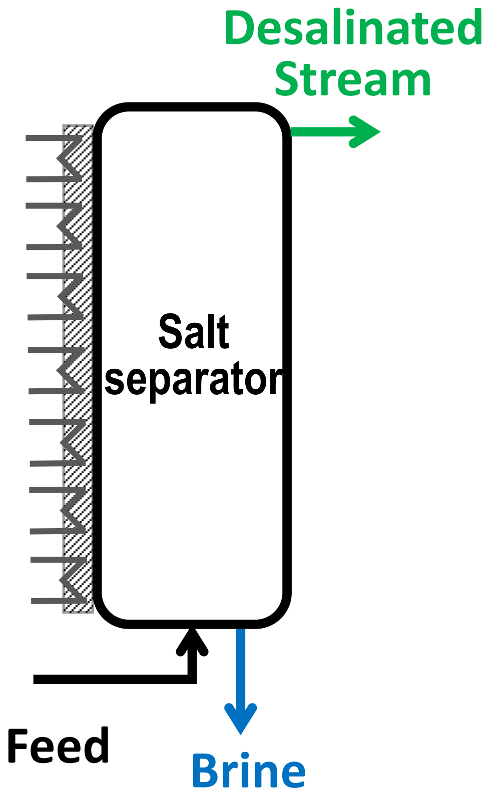
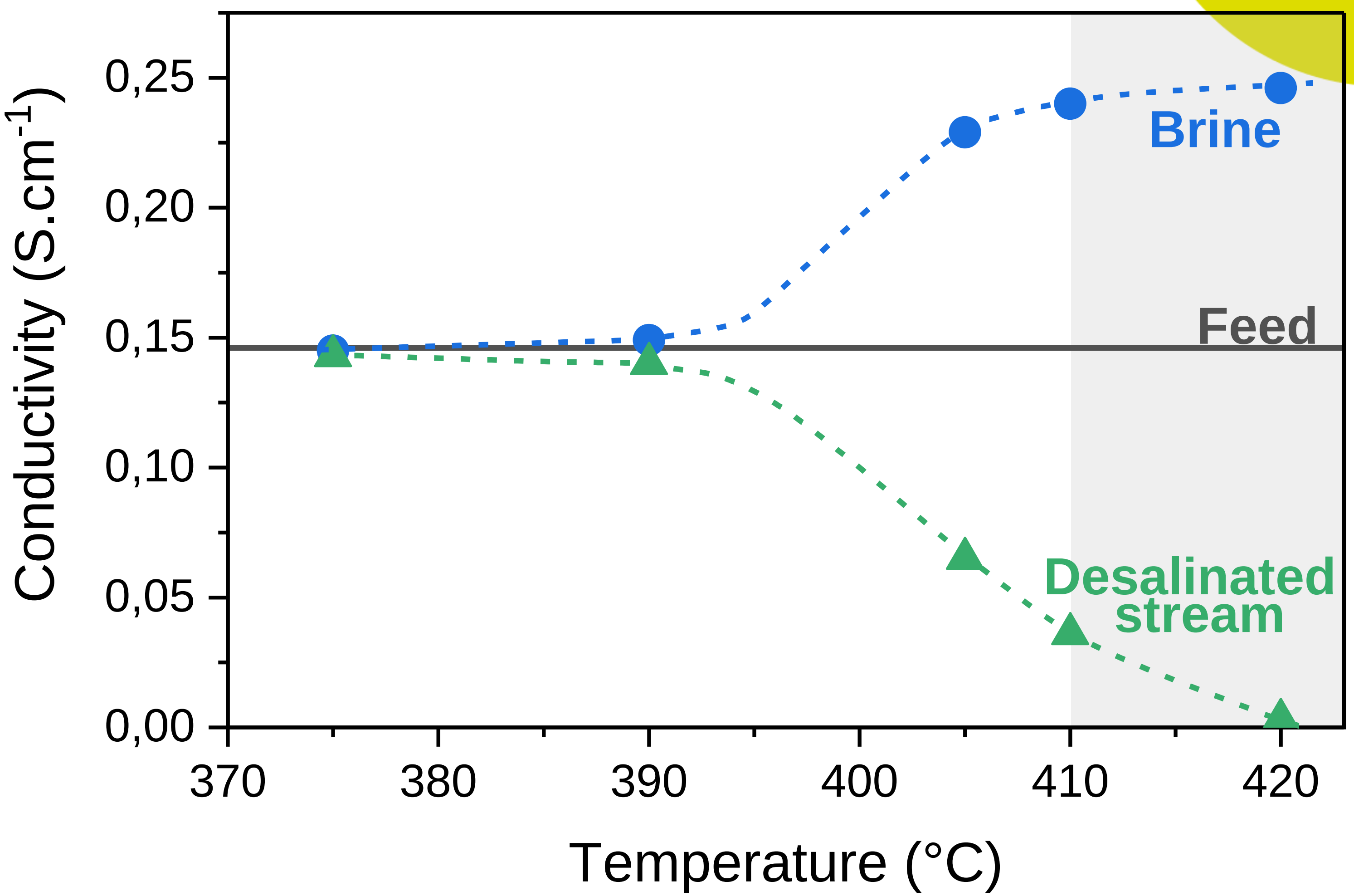
Temperature impact on salt separation

- Acceptable salt separation only above 410°C





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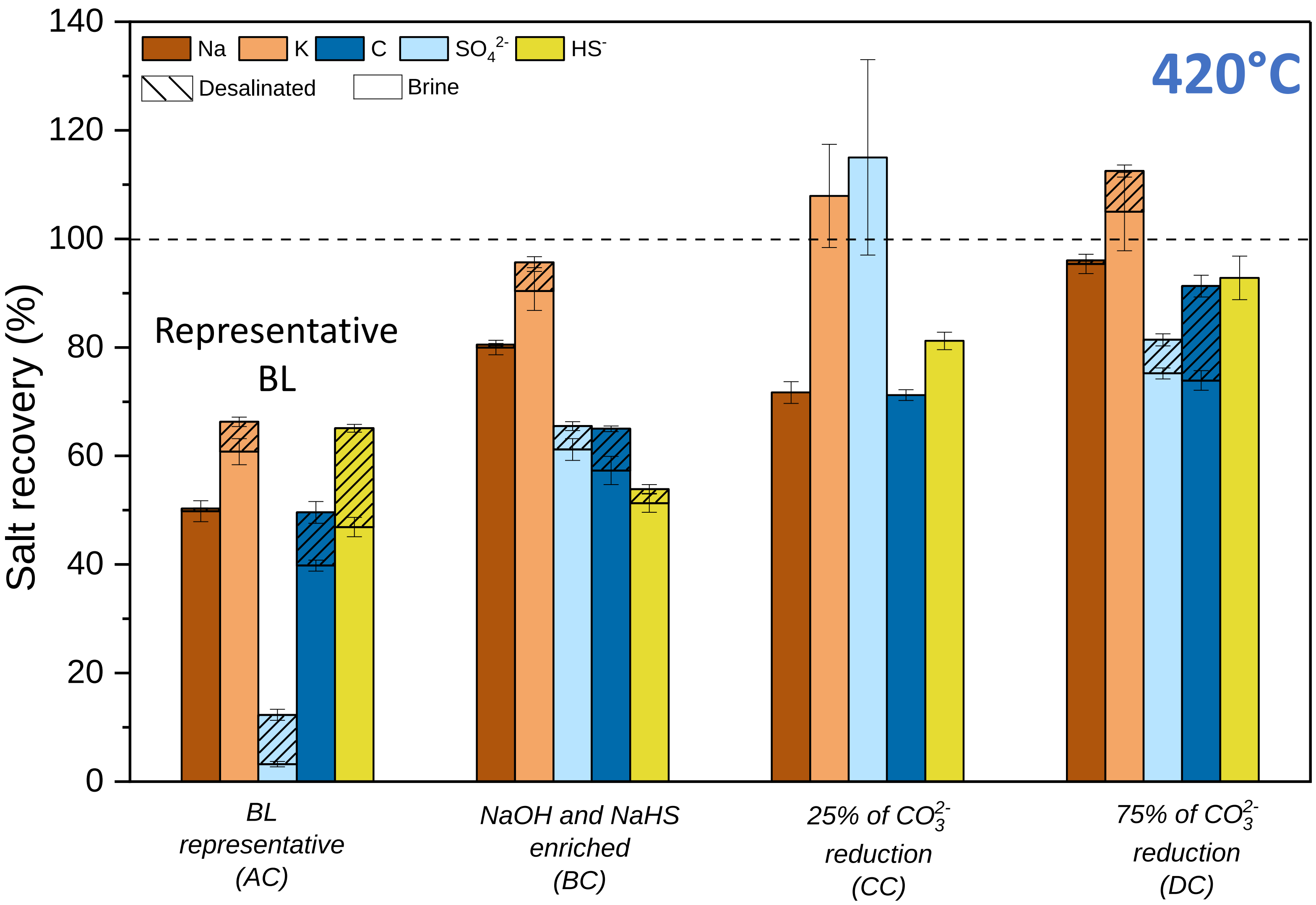
Continuous extraction: model salts



- Plug formed with BL representative model
- No plugs observed with strategy 1&2
- Good recovery efficiency reached with 75% causticization

Canabarro N. I. et al, J. Supercrit. Fluids, accepted

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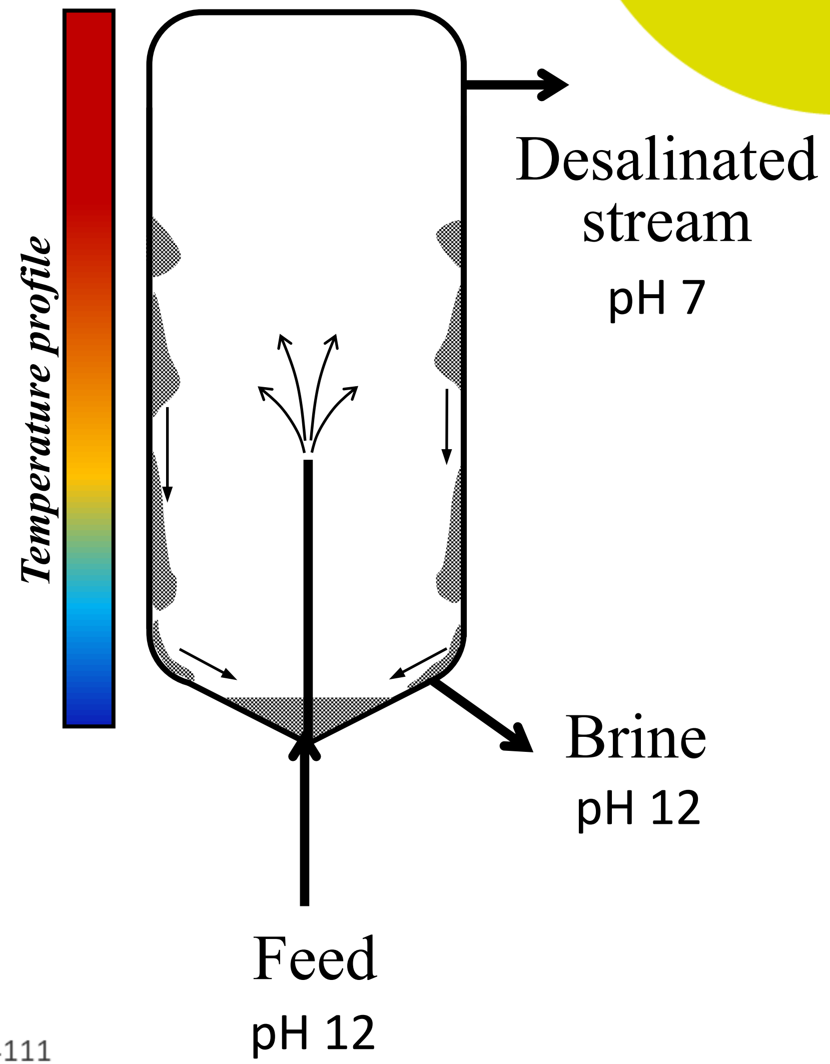
Coupling salt separation & HTL

Feed composition

75%	25%
model salt solution (75% caustization)	hardwood weak BL

- No plug observed
- Large change of pH



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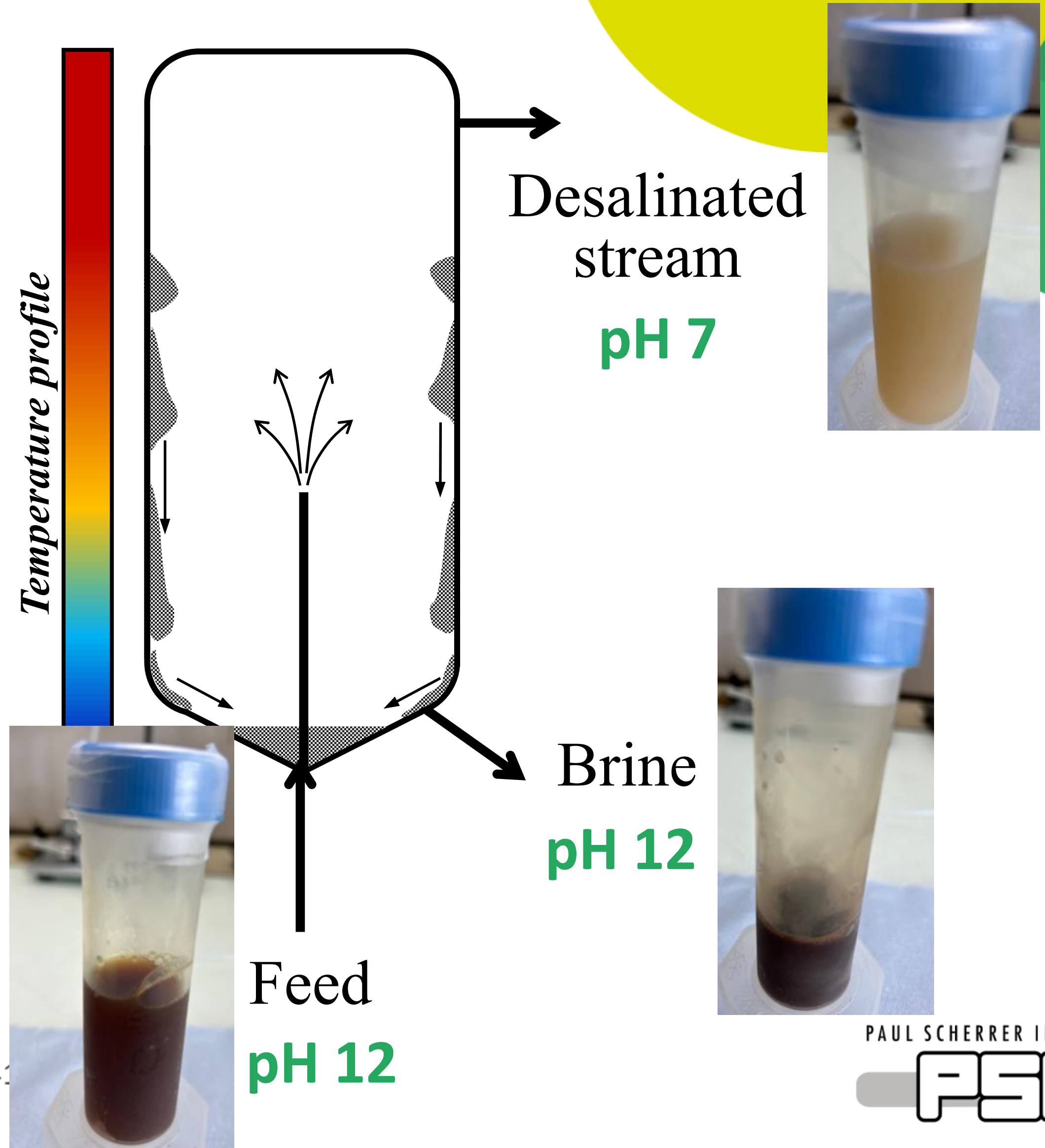

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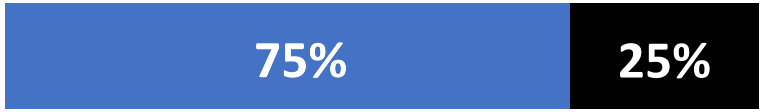
Coupling salt separation & HTL

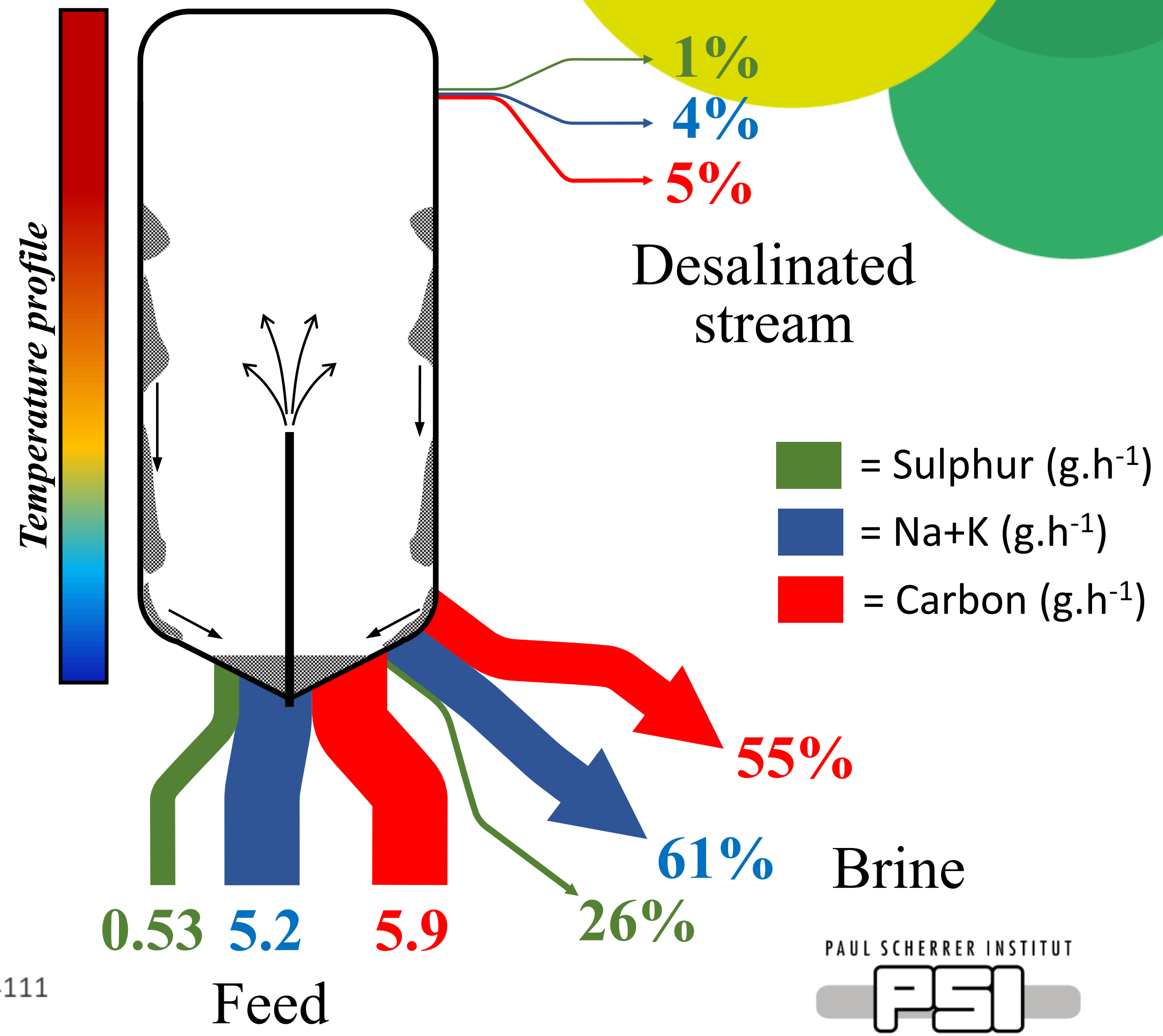
Feed composition



- Biocrude yield in the brine: $15\%_{C\text{-basis}}$
- $C_{biocrude}$ represents 27% of C_{brine}
- Biocrude composition:

C (wt%)	H (wt%)	S (wt%)
53,1	5,1	5,8

Brine: 35wt% of the feed flow



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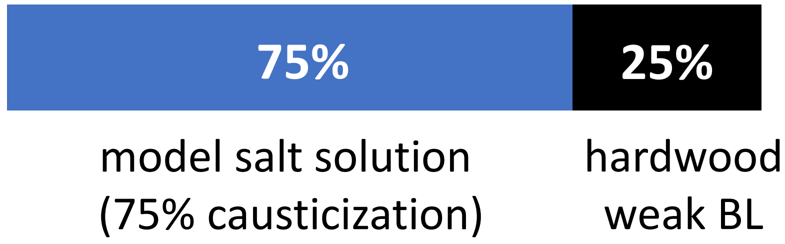
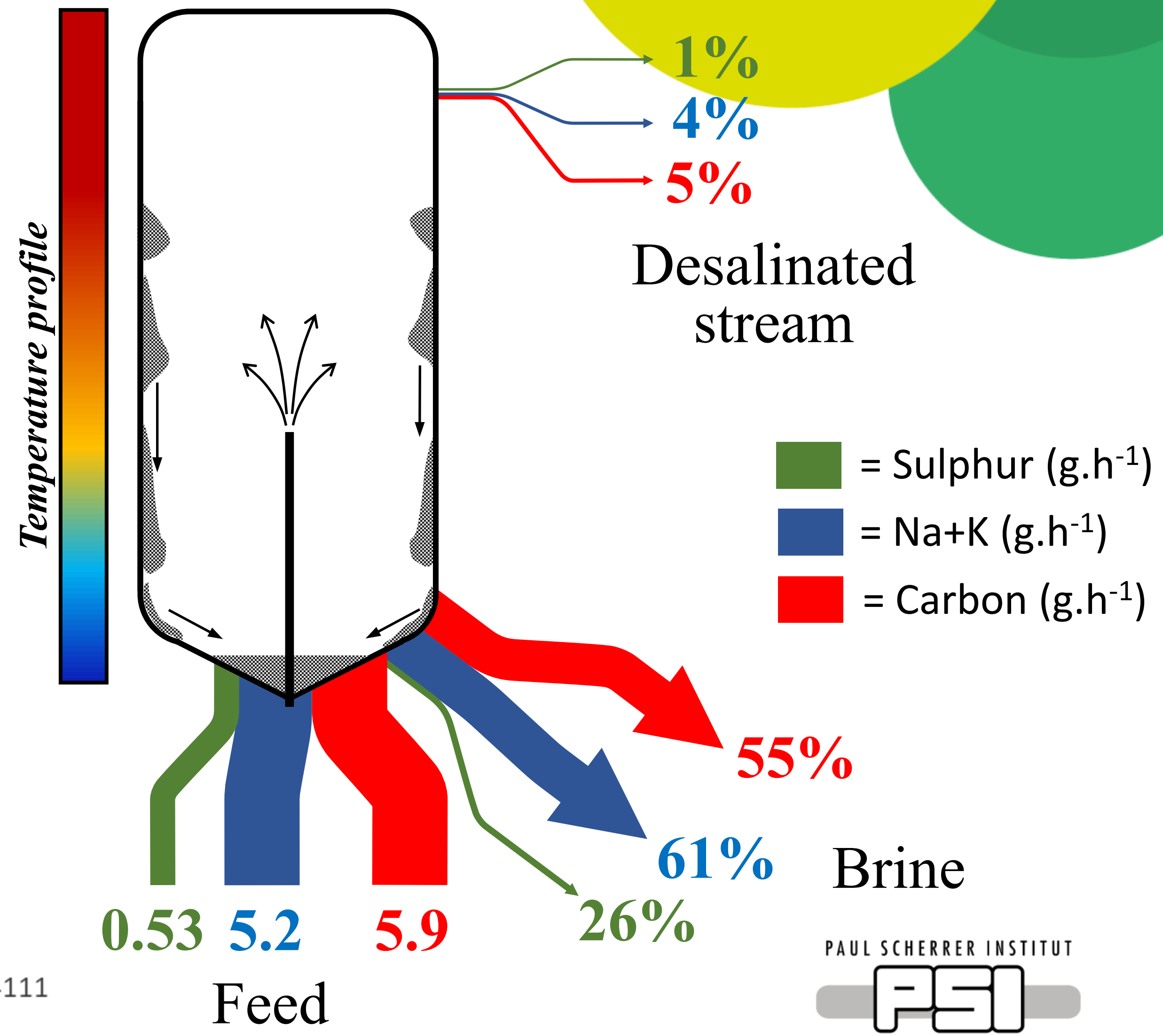
Coupling salt separation & HTL

Feed composition



- Mass balances not closed: loss in the cooled parts
- 61% of cations recovered in the brine
- Very low carbon recovery in the desalinated stream



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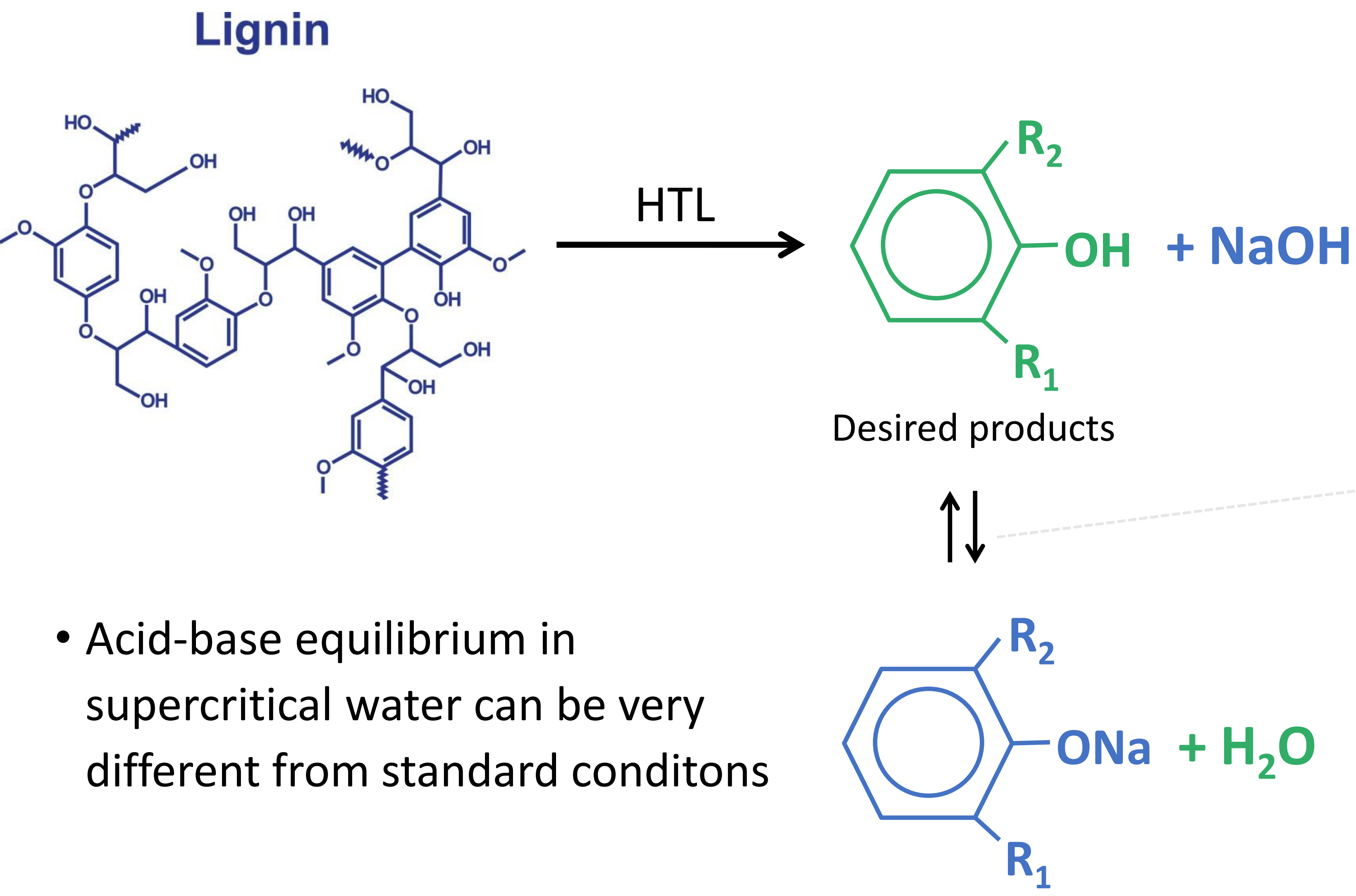
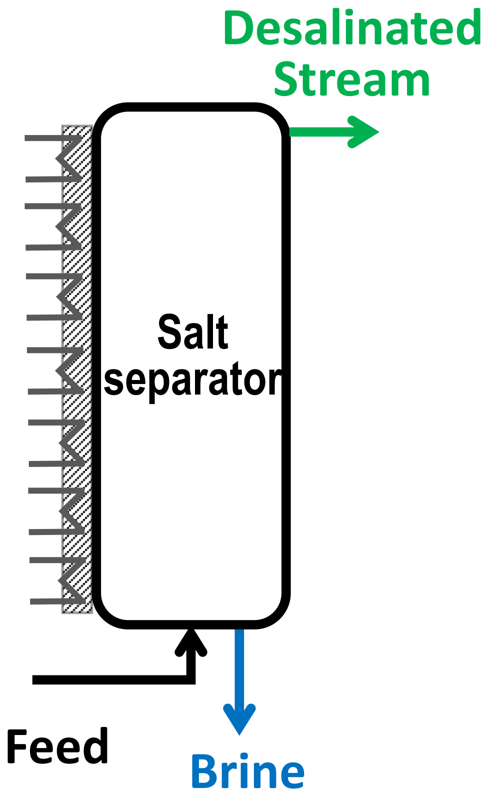
Phase behavior of phenolates?





- Acid-base equilibrium in supercritical water can be very different from standard conditons

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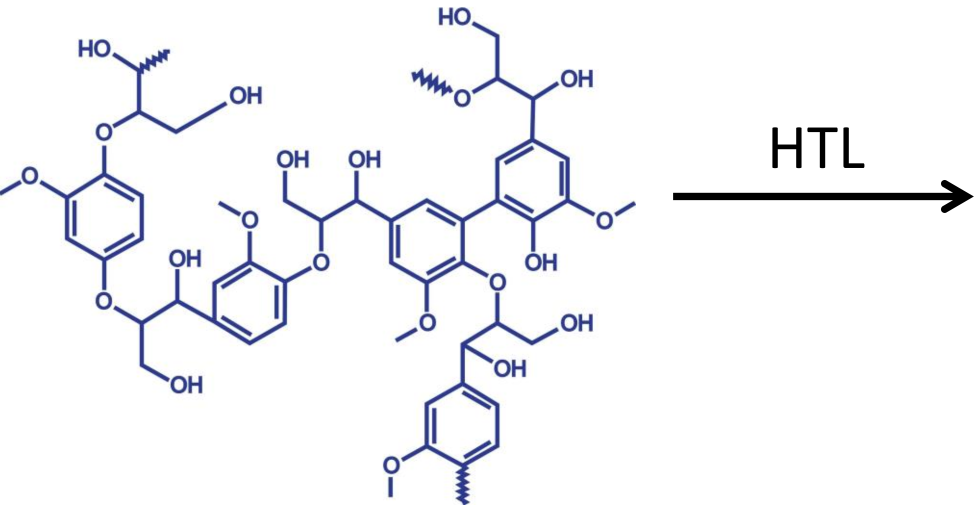
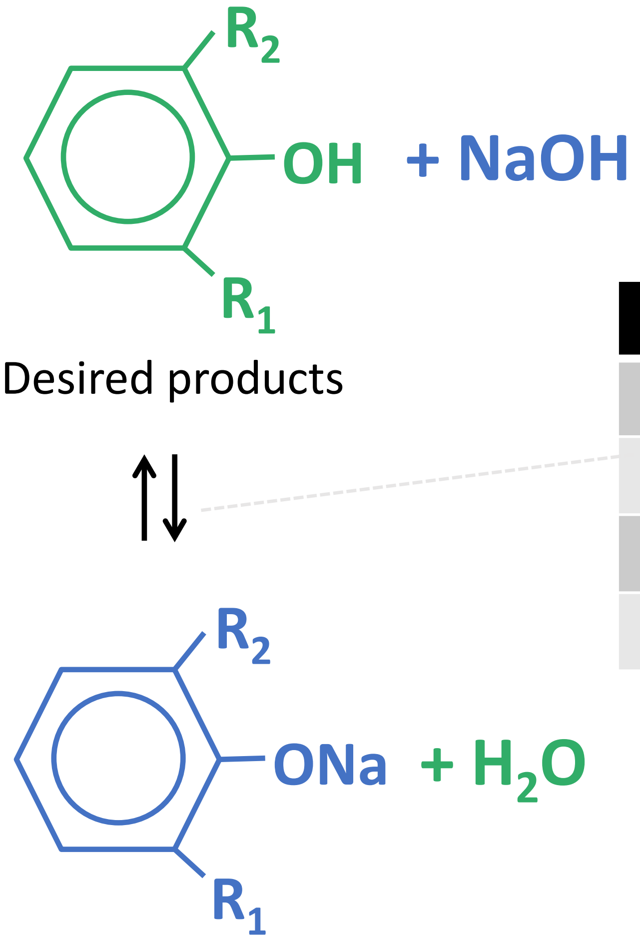
Phase behavior of phenolates?

Lignin





Compounds		pKa
Phenol	$R_1=R_2=\emptyset$	10.0
Guaiacol	$R_1=OMe$; $R_2=\emptyset$	10.0
Syringol	$R_1=R_2=OMe$	9.4
Catechol	$R_1=OH$; $R_2=\emptyset$	9.2 & 12.8

- All aromatic alcohols should be in the form of salts at pH 12-13
  - Do they separate like in the salt separator like other salts?

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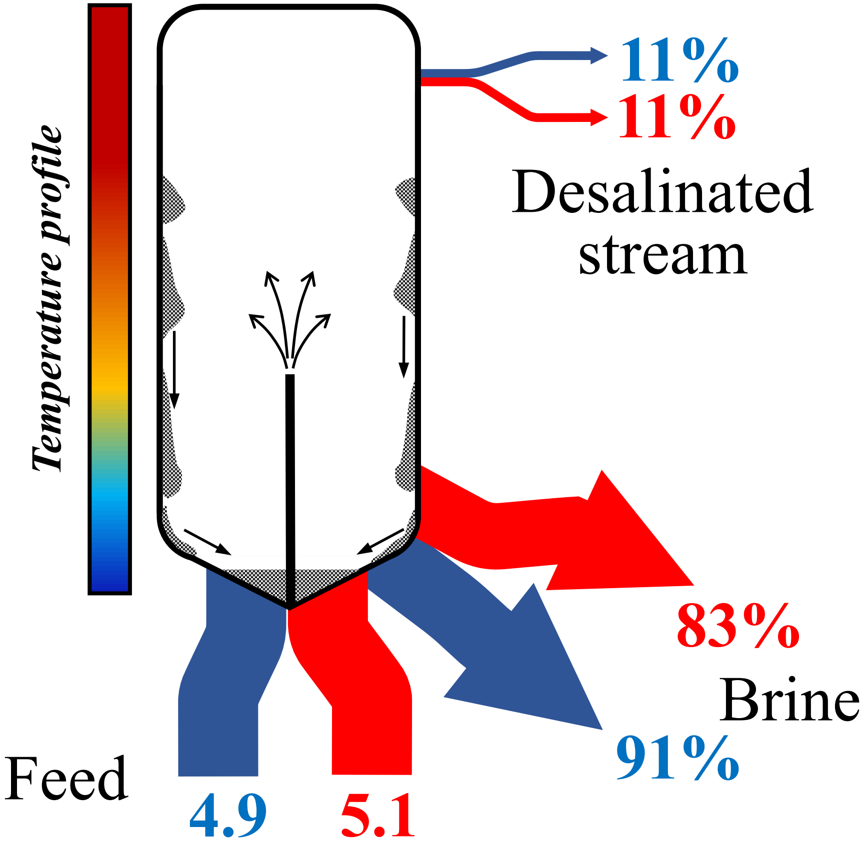
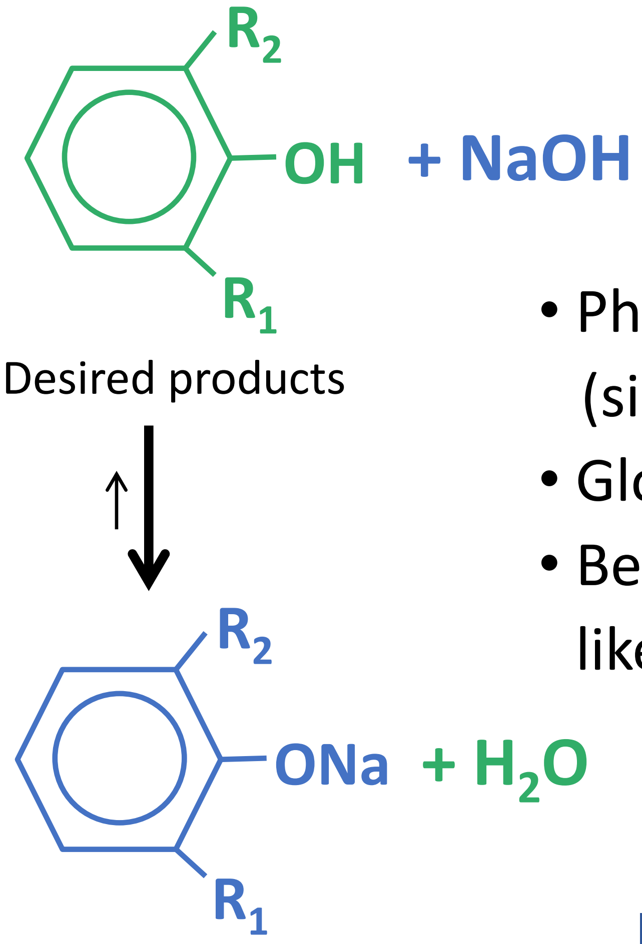
Phase behavior of phenolates?

Feed: acetate-rich model salts, 75% causticized, **0.5wt% phenol**





- Phenolates dominate over phenols (similar to carboxylates)
- Global type 1 phase behavior
- Behavior of polyphenols & phenolic likely similar

= Organic C (g.h-1)

= Total C (g.h-1)

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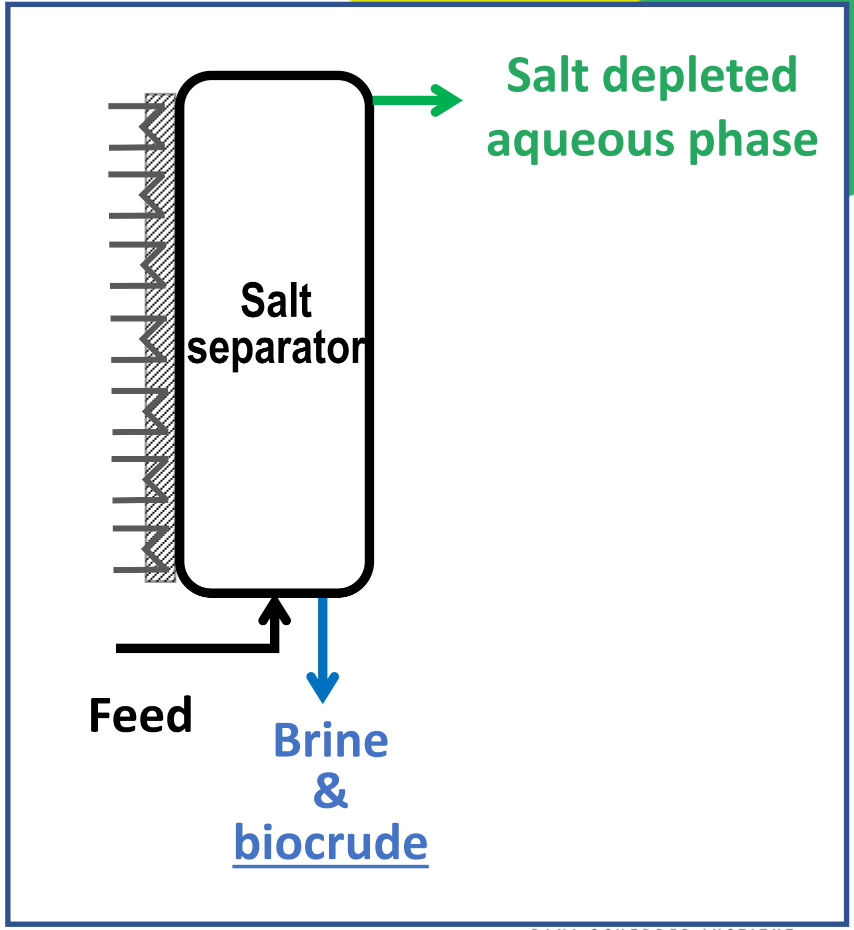
Conclusions

Optimisation of salt separation

- HP-DSC analytical method for the study of high pH solutions
- Two strategies identified to prevent plugging
- Cauterization gives good & steady extraction performance

Coupling HTL & salt separation with black liquor

- Good & steady inorganic salt separation reached
- Temperature range for optimal salt extraction identified
- Phenolic compounds are separated from the mainstream, along with inorganic salts
- Most carbon is extracted in the brine, with only 27% being biocrude



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Thank you!

Get in touch with the project:

- Coordinator: Prof. Dr. Tero Joronen, Tampere University
- Website: www.bl2f.eu

hello@bl2f.eu @BL2F_EU BL2F_EU

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BL2F Partners:

Tampere University

Brunel University London

KIT Karlsruhe Institute of Technology

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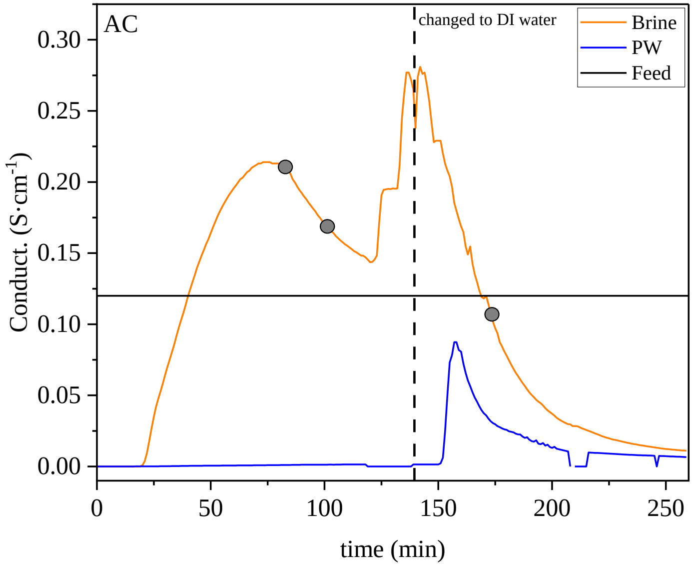
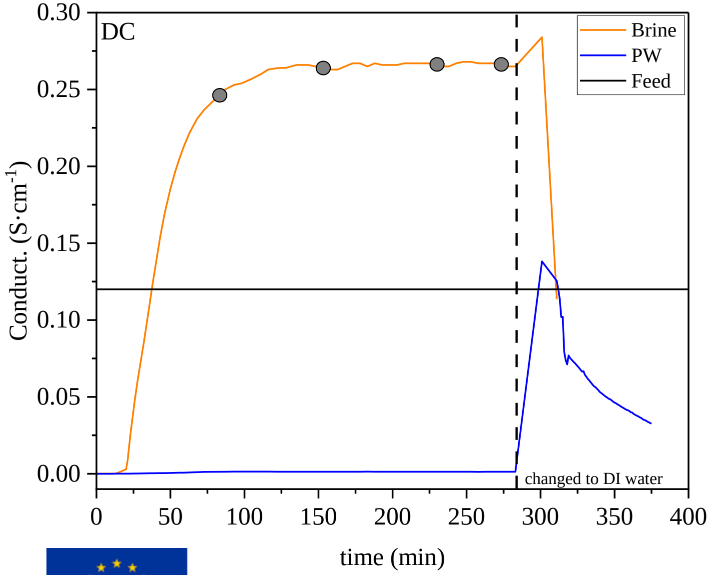
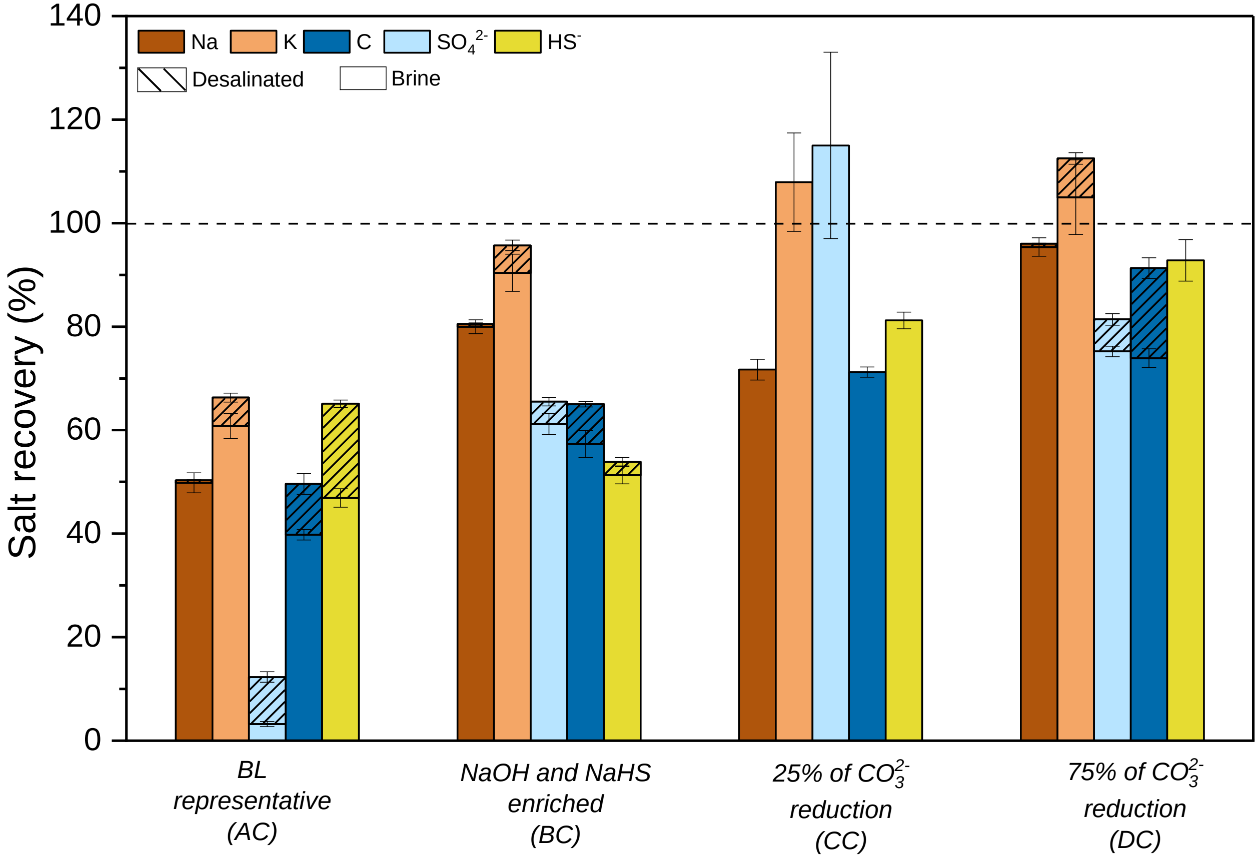
Continuous extraction: model salts



Representative BL



75% carbonate reduction



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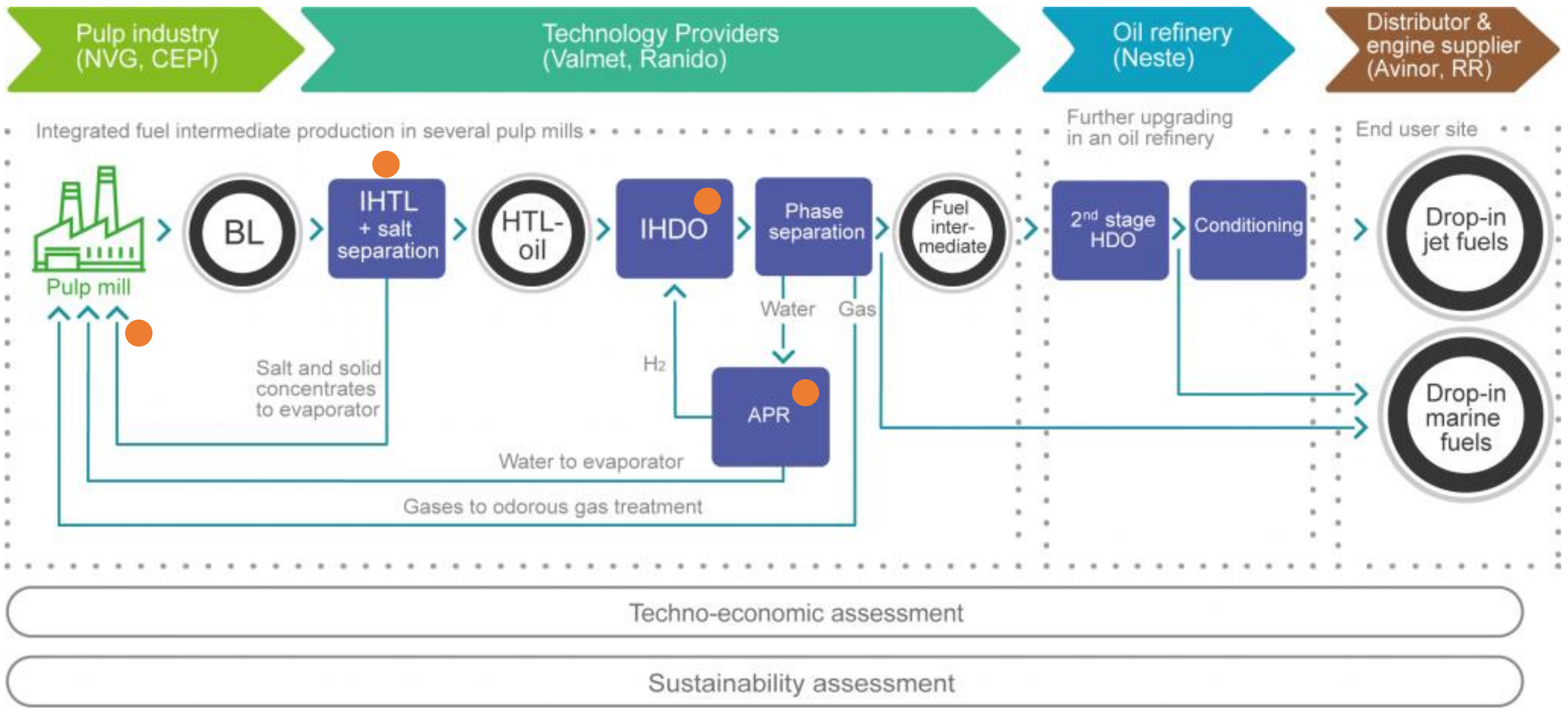
WP2 in the BL2F project

Black Liquor to Fuel (BL2F) is a H2020 project that will transform **Black Liquor** (from Kraft process) into a new, clean biofuel for aviation and shipping.



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● Main project innovations

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