Preliminary Results Salt Separation

BL2F Mid-Term Workshop

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BL2F

Transforming Black Liquor to Biofuel

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

Presentation Overview

- Introduction in salt separation
- Types of salt separation
- HP-DSC Results
  - Crucibles
  - Adjusting NaOH and NaHS
- Summary and future work

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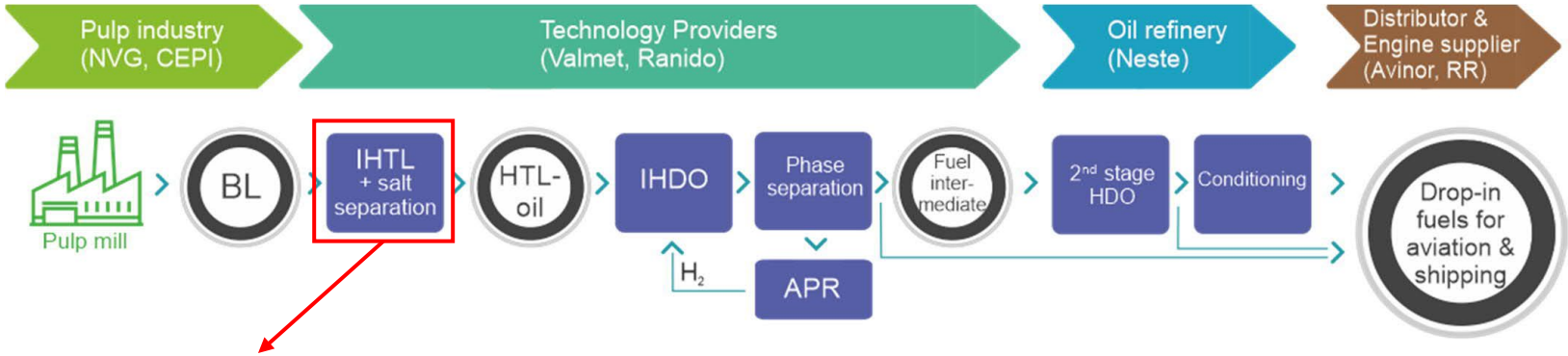
Black Liquor to Fuel (BL2F)



Task 2.1 – Optimisation of Salt Separation from Model Salt Solutions

- Collecting phase equilibria data of model salt solutions by HP-DSC
- Obtaining continuous salt separation efficiencies on Salsan II test rig

Task 2.2 – Optimisation of Salt Separation from BL

Aim – To induce Type 1 salt separation

- Adjusting NaOH and NaHS salt concentrations
- Addition of new salts, such as Na_2HPO_4
- Removal of Type 2 salts

Typical BL salt content ranges from lit.	NaOH wt.%	NaHS wt.%	M_2SO_4 wt.%	M_2CO_3 wt.%	Total wt.%
	0.7 – 3	0.5 – 2.6	0.2 – 1.9	1.6 – 7.0	≈5

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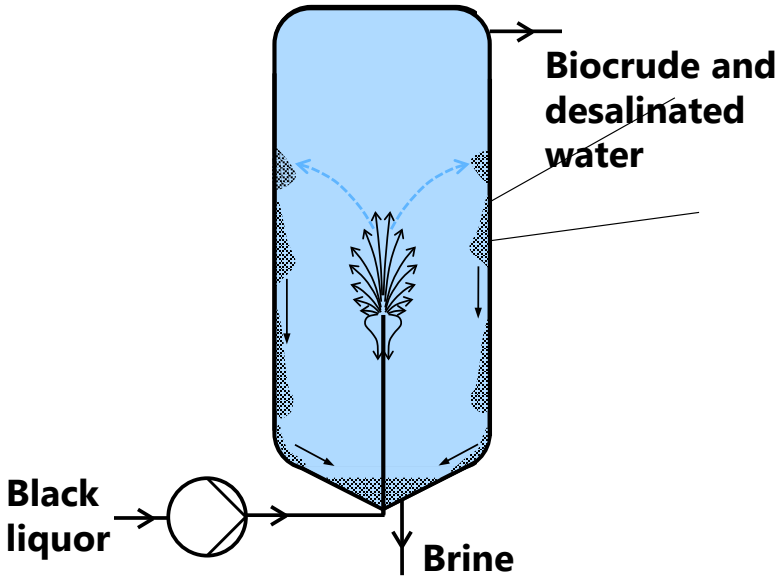
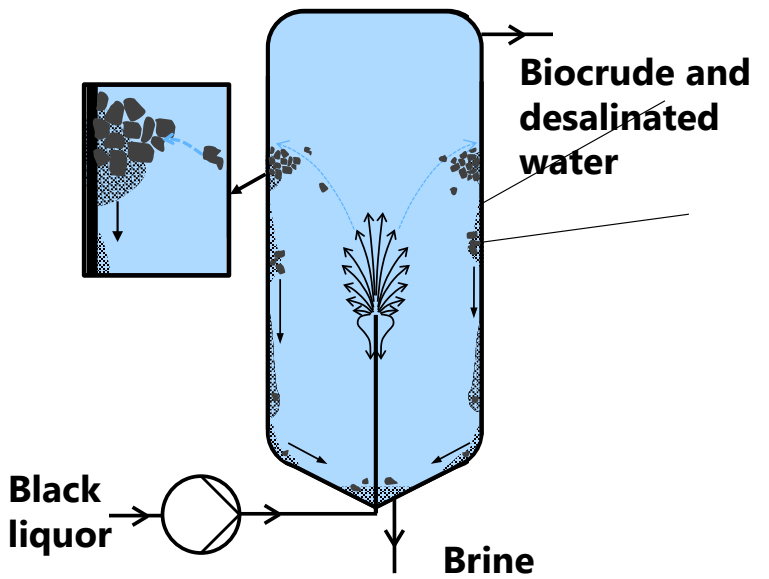
Types of Salt Separation under Supercritical Conditions

Type 1 Salt Separation



Optimal continuous salt separation with Type 1 salts

Type 2 Salt Separation



Sub-optimal continuous salt separation with Type 2 salt precipitation building up on reactor walls

Figures taken from: Runyu Wang, Industrial & Engineering Chemistry Research 2021 60 (10), 4072-4085

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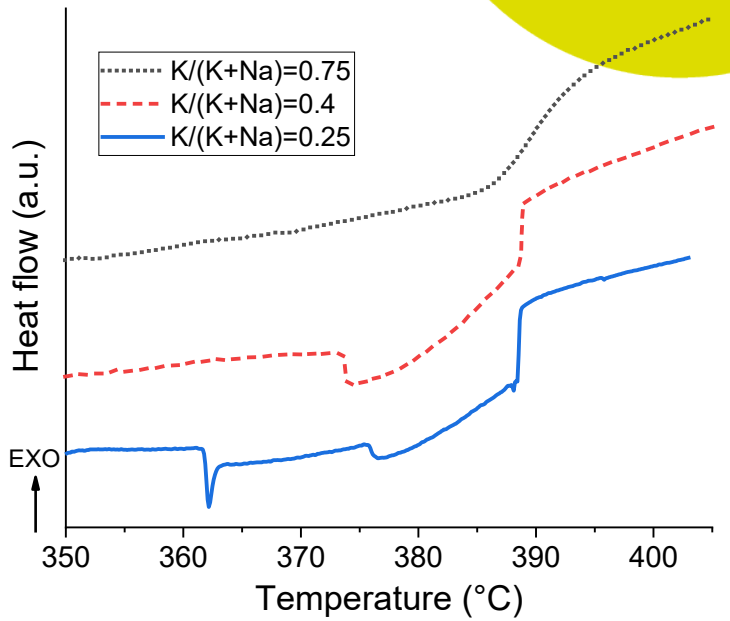
The behaviour of Salts under Supercritical Conditions

Under supercritical conditions single salt-water mixtures can behave one of two ways:

1. Phase separate into a brine rich phase and a desalinated phase – **Type 1** behaviour
2. Undergo precipitation, forming solid salt and desalinated phase – **Type 2** behaviour

Mixtures of salts is more complex, with no accurate model to predict the phase behaviour

- Mixtures of solely Type 1 can exhibit Type 2 behaviour and *vice versa*
- Factors to take into account is the composition of individual salts, as well as the temperature and pressure
- It is currently impossible to accurately predict salt the behaviour of mixtures



Increasing the concentration of larger cations, such as potassium has shown to promote Type 1 salt separation.

- Not ideal for the Kraft process due to difficulty in recovery

Figure taken from: Runyu Wang, Industrial & Engineering Chemistry Research 2021 60 (10), 4072-4085

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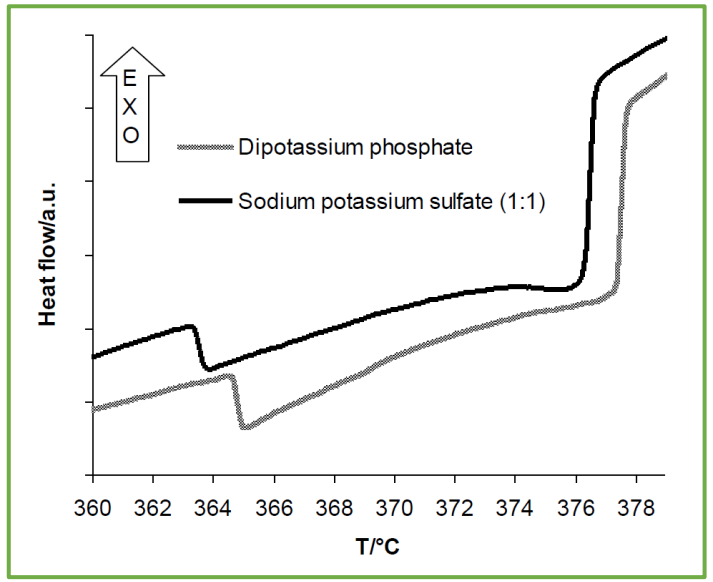
HP-DSC Type 1 and Type 2 Salt Behaviour

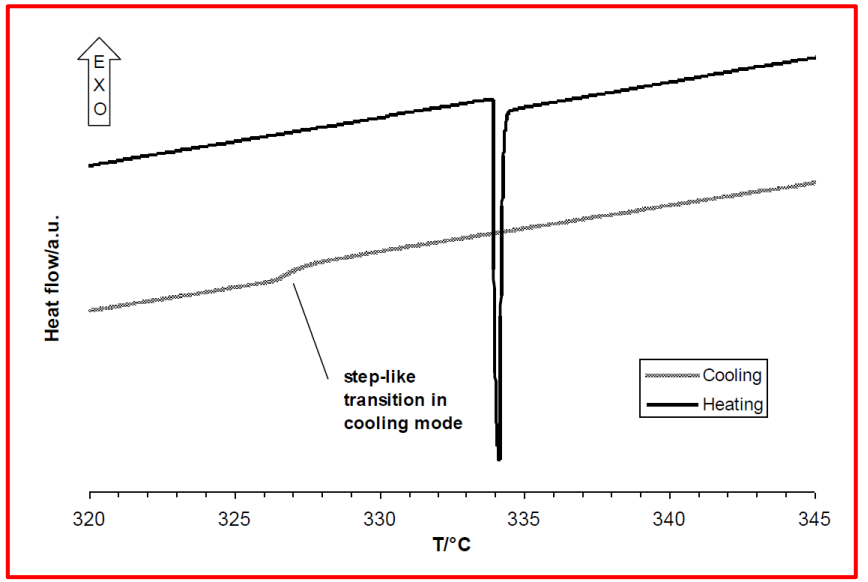
Type 1

- Phase separation into brine rich and desalinated phases
- Endothermic step – heating
- Type 1 + Type 1 ≠ Type 1



Type 2

- Precipitation of salts, due to a rapid drop in dielectric constant
- Sharp endothermic peak – heating
- Type 2 + Type 2 ≠ Type 2



Figures taken from: Reimer, J., Biomass Related Salt Solutions at Hydrothermal Conditions. 2015, ETH Zurich.

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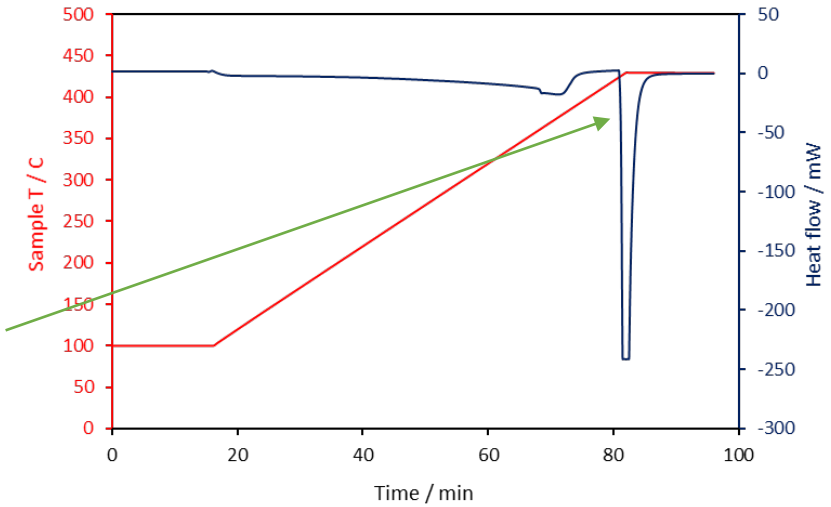
HP-DSC Crucibles

Inconel Crucibles

- Inconel crucibles regularly leaked with mode salt solutions
- Leakage observed by large exothermic peak
- Leakages typically occurred above at supercritical conditions
- Corrosion was visible on the crucibles
- Unable to create a dataset



HP-DSC conditions

- Temperature ramp 0.1 °C/min
- Crucibles filled to a density of 0.3 kg/m^3

Titanium Crucibles

- Titanium crucibles were found to be the best alternative option
- Crucibles pre-treated in 5M NaOH for 24h, washed and annealed at 600 °C 1 h in a furnace
- No signs of leakage or external corrosion

In-house made
Titanium crucibles
Grade 5

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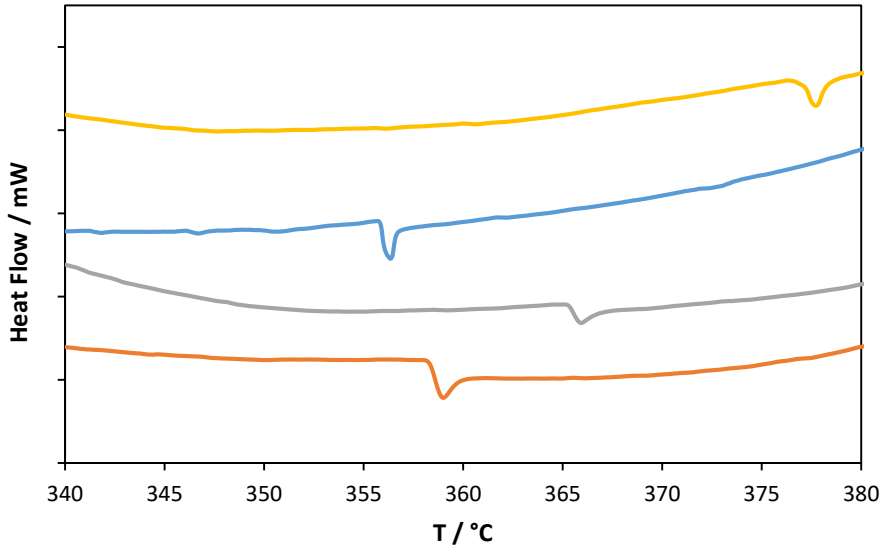
HP-DSC Data of Model Salt Solutions w/o Organics



- 3.5 wt.% NaOH, 1.2 wt.% NaHS
- 1.2 wt.% NaHS
- 3.5 wt.% NaOH
- Reference

- Increasing the NaOH results in increasing the crystallisation temperatures, Type 2
- Excess NaHS causes a slight drop in the crystallisation temperature
- Increasing both NaOH and NaHS sees significant increase in Type 2 transition temperature
- **Alternative strategy required to induce Type 1 salt separation**

Model Salt Solution from Characterisation – Reference Point

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

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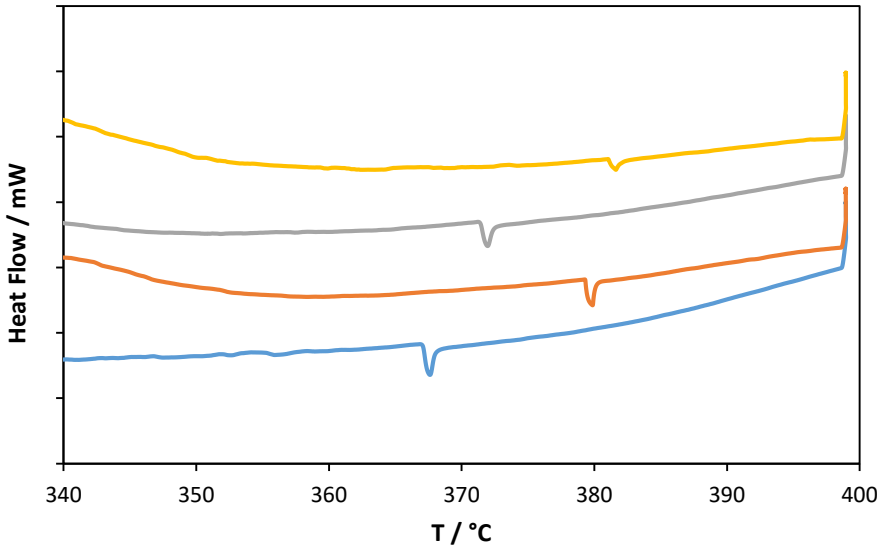
HP-DSC Data of Model SS with Organics

Model Salt Solution Containing Organics

- Organics added in the form of metal acetate, chosen to avoid complex phase transitions
- Quantity of acetate calculated from remaining Na and K from characterisation of BL, and subtracting remaining sulphur content

Model Salt Solution including organics from Characterisation – Reference Point

Salt	wt.% in pristine BL	g/kg	mmol/kg
NaOH	1.74	17.4	435.0
NaHS	0.51	5.1	91.0
Na_2SO_4	0.40	4.0	28.4
Na_2CO_3	1.45	14.5	137.2
K_2CO_3	0.27	2.7	19.6
$NaCH_3CO_2$	2.91	29.1	354.7
KCH_3CO_2	0.24	2.4	24.5



- 3.5 wt,% NaOH, 1.2 wt.% NaHS
- 1.2 wt.% NaHS
- 3.5 wt.% NaOH
- Reference w/ organics

- The addition of acetate to the model solutions results in all transitions shifting to higher temperatures
- Type 1 behaviour is still observed with the extraction of CO_3^{2-} in the presence of organics

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Summary and Future Work

Phase Equilibria Data

- Titanium crucibles are best suited for testing BL model salt solutions
- Increasing the NaOH and NaHS salt content has minimal impact on inducing Type 1 behaviour
- Alternative strategies are needed to be explored to induce Type 1 salt behaviour

Future Work

- Testing salt extraction efficiency under continuous conditions on Salsan II test rig
- Experimental work hopefully to commence in February with last few technical problems being solved
- Initial experiments:
  - Reference model salt solution w/o organics
  - High NaOH and NaHS mixtures
- Repeat experiments with organics
- Upgrading of Salsan II to handle BL
  - Initial experiments with dilute BL and progressively increasing the concentration

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Brunel University London

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Thank you!

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