On the fundamentals of supercritical water salt separation and concomitant HTL using black liquor

BL2F Summer school - KIT

13-06-2023 David Baudouin ::: Paul Scherrer Institute

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Wet biomass valorization

 Growing demand for jets or heavy duty transport but no alternative to chemical energy carriers



Data from the international air transport association (IATA) and from the United Nations conference on trade and development (UNCTAD) Huge amounts of wet biomass & wastes not valorized 12000 80% η_{chem} composition (Vol% dry) 70% 10000 60% (^sem/la) VHJ ک 4000 8000 50% (%) ^m LHV, humid 40% Jche 30% gas 20% U 2000 CH 20% 30% 50% 60% 70% Water content (w%) **Modeling - Fast Internally Circulating Fluidized Bed (FICFB) Technology** Conventional processes yield very low thermal • efficiencies

Schuster et al., Bioresour. Technol. 77 (2001) 71





Hydrothermal valorization of wet biomass

• Broad variety of chemical energy carriers possible





This project has received funding from the

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

Types of Salt Separation under (near)**Supercritical Conditions**

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





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Optimal continuous salt separation with Type 1 salts

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

Wang et al., Ind. Eng. Chem. Res. 60 (2020) 4072





Hydrothermal valorization of wet biomass

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





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Hydrothermal gasification at PSI



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Hydrothermal liquefaction at PSI



Hydrothermal processes at PSI

The Energy System Integration (ESI) platform at PSI







Hydrothermal processes at PSI

The Energy System Integration (ESI) platform at PSI







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 (semi)continuously remove salts from main stream

- By inducing Type 1 salt separation
 - Adjusting NaOH and NaHS salt concentrations
 - Addition of new salts, such as Na₂HPO₄
- Co-feed solids to prevent fouling

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Typical BL salt content ranges from lit.	NaOH	NaHS	M ₂ SO ₄	M ₂ CO ₃	Total
	wt.%	wt.%	wt.%	wt.%	wt.%
	0.7 – 3	0.5 – 2.6	0.2 – 1.9	1.6 – 7.0	≈5



High Pressure Dynamic Scanning Calorimetry (HP-DSC)

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



Reimer, J. et al., Biomass Related Salt Solutions at Hydrothermal Conditions, PhD Thesis 2015, ETH Zurich.





Why using HP-DSC & choice of crucibles

Mixtures of salts is more complex

- No accurate model to predict the phase behaviour
- Mixtures of solely Type 1 can exhibit Type 2 behaviour and vice versa
- Composition of individual salts, temperature and pressure affect phase behavior

Choice of material for crucibles

- Inconel not compatible with reductive supercritical water(regular leak)
- Leakages typically occurred above at supercritical conditions
- *Titanium* = good alternative, no leak
- Crucibles pre-treated in 5M NaOH for 24h, washed and annealed at 600°C1 h in a furnace





Commercial Inconel

In-house made Titanium crucibles Grade 5



| HP-DSC conditions | Temperature ramp 0.1 °C/min | Crucibles filled to a density of 0.3 kg/m3

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Influence of K/Na on salts phase behavior



Salt	[Salt] mmol.L ⁻¹	
M ₂ SO ₄	45	
M ₂ CO ₃	152	
MOH	182	
M ₂ S	102	
M= N	a or K	

- Proof of occurrence of both crystallization and liquid-liquid immiscibility phenomenon
- High K/Na prevents solid formation

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Influence of K/Na on salt sep. efficiency

• Concentration of salts in the brine, but salt start precipitating after some time



Influence of K/Na on salt sep. efficiency

- At high K/M ratio ≥ 0.25-0.4: no plug formed anymore
- Steady salt recovery in brine > 90%



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



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 ₂ SO ₄	0.40	4.0	28.4
Na ₂ CO ₃	1.45	14.5	137.2
K ₂ CO ₃	0.27	2.7	19.6
Total	4.4	43.8	711.1





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







- Selective removal of CO_3^{2-} (e.g. with Ca^{2+}) is a promising approach
- Global type 1 behavior observed when feed causticized







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The addition of acetate (stable organic) to the model solutions results in

- All transitions shifting to higher temperatures
- Type 1 behaviour is still observed with the extraction of CO₃²⁻ in the presence of organics





Test rig for continuous extraction tests coupled to HTL



Hydraulic Flow residence time (mL.min⁻¹) (min) 1 ≈15 6.3 2.8 20 ≈1





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Continuous extraction: model salts



Representative BL







Continuous extraction: model salts



Effect of temperature on salt sep.

Model salt solutions with 75% of carbonate reduction (Exp GC)







Pinewood HTL waste water valorization

• 44% of C lost in the brine stream



D. Baudouin, et al., ACS Engineering Au 1 (2021) 134



Conditions: 290bars, Separator: 380-460 °C, Reactor: 380-400 °C | 22h operation, Feed: 0.9kg/h, 8wt% DM |



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 764734



Salt separator: selectivity on organics



Identification of organics lost in the brine

• 75% of carbon in the brine identified as carboxylate: energy loss



Optimizing process conditions

Improve biogas yield: favor decarboxylation (t_{retention}/Temperature)





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Summary and Future Work

Salt separation

- Various strategies allowed for preventing salt deposition/fouling
- Carbonate selective extraction (cauterization) is the most attractive one
- Organic salts efficiently separate in SCW, conditions can be optimized to decompose them

Ongoing Work: optimization of HTL & salt separation

- Further tests with real black liquor
- Identifying an optimal temperature and residence time for HTL & salt separation
- Detailed analysis of streams for organic composition overview







BL2F Partners:







VTT





Valmet > П









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Thank you!

Get in touch with the project:

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Hydrothermal gasification at PSI



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



- 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

- 1.2 wt.% NaHS

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

- 3.5 wt.% NaOH
- Reference

Model Salt Solution from Characterisation – Reference Point

	wt.% in		
Salt	pristine BL	g/kg	mmol/kg
NaOH	1.74	17.4	435.0
NaHS	0.51	5.1	91.0
Na ₂ SO ₄	0.40	4.0	28.4
Na ₂ CO ₃	1.45	14.5	137.2
$K_2 CO_3$	0.27	2.7	19.6
Total	4.4	43.8	711.1





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/ organic decomposition
- Quantity of acetate calculated from remaining Na and K from characterisation of BL, and subtracting remaining sulphur content

370

T/℃

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 ₂ SO ₄	0.40	4.0	28.4
Na ₂ CO ₃	1.45	14.5	137.2
K ₂ CO ₃	0.27	2.7	19.6
NaCH₃CO₂	2.91	29.1	354.7
KCH ₃ CO 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 CO₃²⁻ in the presence of organics



Heat Flow / mW

340

350

360

380

390

400

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