Inorganic salts extraction from Black Liquor under hydrothermal liquefaction conditions

Nicholas Canabarro[1], Darius Yeadon[1], Frédéric Vogel[1,2], David Baudouin[1],

[1]Bioenergy and Catalysis Laboratory (LBK), Paul Scherrer Institute, 5232 Villigen, Switzerland; nicholas.islongo-canabarro@psi.ch, david.baudouin@psi.ch, frederic.vogel@psi.ch;

[2]Fachhochschule Nordwestschweiz, 5210 Windisch, Switzerland;

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1. Aim and approach used

This work aims to assess the ability of PSI supercritical water (SCW) salt separator to desalinize inorganic compounds from complex black liquor model salt solutions. This work was performed in the frame of the H2020 project Black Liquor to Fuel (BL2F, grant 884111) which aims at producing jetfuels from black liquor through Hydrothermal Liquefaction (HTL). More precisely, an SCW salt separation step is aimed to be integrated to HTL process. Strategies to continuously extract salts from the brine have therefore been evaluated to allow a smooth process, which are presented in this work. A fundamental study of model salt solution phase behaviour by isochoric high-pressure differential scanning calorimetry (HP-DSC) was performed to reach these goals. Batch tests screened the conditions. Distinguished strategies were adopted to induce Type 1 salt behaviour. Lastly, the salt solutions that presented the most promising phase behaviour were tested in our continuous salt separator test rig under hydrothermal conditions to confirm the results obtained with the HP-DSC study. Table 1 shows the model salt solutions investigated by HP-DSC, while Table 2 shows the model salt solutions tested in the continuous salt separation process under hydrothermal conditions.

Table 1. Composition of the inorganic model salt solutions. Experiment A is based on the characterisation of Black liquor (BL).

		Experiment								
Salt	**Unit**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
NaOH	wt.%	1.74	3.49	1.72	3.49	1.75	1.73	2.05	2.34	2.63
NaSH	wt.%	0.51	0.50	1.20	1.20	0.51	0.51	0.51	0.51	0.51
Na_2SO_4	wt.%	0.42	0.43	0.41	0.40	0.41	0.40	0.42	0.41	0.40
Na_2CO_3	wt.%	1.44	1.50	1.45	1.46	0.35	0.75	1.09	0.72	0.39
K_2CO_3	wt.%	0.28	0.27	0.27	0.27	0.07	0.15	0.20	0.14	0.06
KOH	wt.%							0.06	0.11	0.17

Table 2. Detail of continuous salt separation experiments performed with salt model solutions.

		Experiment							
Salt	**unit**	**AC[1]**	**BC**	**CC**	**DC**	**EC**	**FC**	**GC**	**HC**
Na^+	$mol.L^{-1}$	0.86	1.40	0.86	0.86	0.86	1.40	0.86	0.86
K^+	$mol.L^{-1}$	0.04	0.04	0.04	0.04	0.04	0.04	0.06	0.04
OH^-	$mol.L^{-1}$	0.43	0.87	0.67	0.53	0.43	0.87	0.67	0.53
HS^-	$mol.L^{-1}$	0.09	0.21	0.09	0.09	0.09	0.21	0.09	0.09
SO_4^{2-}	$mol.L^{-1}$	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
CO_3^{2-}	$mol.L^{-1}$	0.15	0.15	0.04	0.11	0.15	0.15	0.04	0.11
$CH_3CO_2^-$	$mol.L^{-1}$	-	-	-	-	0.37	0.37	0.37	0.37
Feed flow rate	$g.min^{-1}$	6.39	6.40	6.25	6.14	6.33	6.43	6.31	6.21
Brine flow rate	$g.min^{-1}$	1.98	2.03	1.91	2.01	1.27	1.82	1.80	2.52
Feed conduct.	$mS.cm^{-1}$	110	190	150	120	110	190	150	120

[1]Based on black liquor composition (Wang et al., 2021). For all the experiments, the first four heaters were set to 450 °C and the last four ones were set to 400 °C (see Figure 1). The pressure for all experiments was kept at 250±5 bars.

2. Scientific innovation and relevance

Concerns regarding climate change and its environmental impacts have inspired global efforts to reduce the use of fossil fuels and replace it with biofuels (Fokaides and Christoforou 2016). Several studies have pointed to the importance of biomass in drop-in biofuels production, particularly jetfuels, (Alherbawi et al. 2021; Fu and Turn 2019; Martinez-Villarreal et al. 2022) and stressed the necessity for improvement in its utilization. The suitable use of these by-products may lead many industrial processes to become energetically self-sufficient or, at least, can contribute to improving the global process's energy efficiency (Batlle et al. 2022). In the pulp mill industry, the Kraft process is the most common to produce pulp from lignocellulosic biomass. It produces an aqueous side stream called black liquor (BL) which consists of a mix of lignin, hemicellulose, hydrocarboxylates and inorganic salts (cooking salts and reaction products), with a dry matter content of ca. 15−20 wt. %.(Wang et al. 2021; Lappalainen et al. 2020) Hydrothermal processes such as liquefaction (HTL) and gasification (HTG) are promising technologies that have great potential in valorising such wet biomass into bio-crude and biogas, respectively, without the need for energy-demanding water evaporation. Under hydrothermal conditions, the organic matter present in the wet biomass is transformed into biofuels while the inorganic compounds are prone to precipitation under the conditions used and foul heat exchangers and clog pipes (Wang et al. 2021; Schubert, Regler, and Vogel 2010a; 2010b).

Understanding the behaviour of salts under HTL conditions plays an important role in integrating the salt separation with HTL process. This understanding is relevant to develop strategies to prevent fouling and to allow extracting them from the mainstream (bio-crude and process water). Valyashko (2006) who has derived 26 full-phase diagrams for binary salt-water systems has classified the phase behaviours of salts in water. Following this classification, salts can be classified into two main categories: Type 1 and Type 2 salts. Type 2 salts precipitate when saturated, while type 1 forms a second liquid phase rich in salts. Therefore, induce the Type 1 behaviour seems to be a promising strategy to prevent salts precipitation in SCW conditions. At PSI, our group has been working on the analysis of multicomponent salt solution behaviour in the frame of H2020 project Black Liquor to Fuel (BL2F, grant 884111). Different strategies to prevent salt precipitation has been proposed and promising results have been achieved aiming to integrate salt separation for HTL of black liquor.

3. Preliminary Results

3.1. Studying model salt solutions by HP-DSC

Figure 1 shows the heat flow curves for the different strategies adopted to induce Type1 salts behaviour in the model salt solutions The results obtained that the reference model (experiment A) salt solution exhibited Type 2 behaviour, with precipitation of insoluble salts at supercritical conditions. The strategy of increasing NaOH and NaHS (Figure 1.1) to induce Type 1 salts behaviour proved to impact the temperature at which the salts precipitate but did not prevent the precipitation in the concentrations studied (realistic for the Kraft process). The model salt solutions exhibited Type 1 behaviour after removing 75% of carbonate, which seems to be a promising strategy to have a smooth operation of a continuous desalination process.

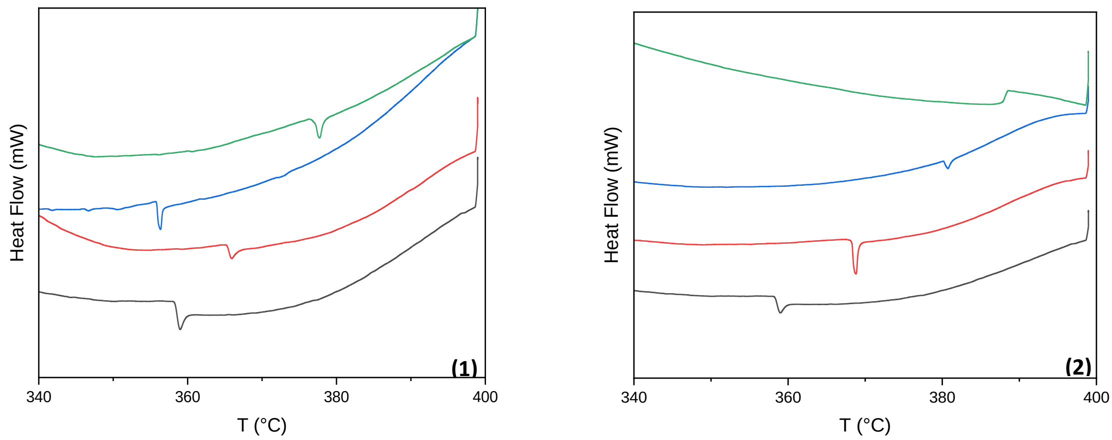

Figure 1. Heat flow curves traces for the model salt solutions assessed in this study. (1) Inducing Type 1 salt behaviour by varying the concentrations of NaOH and NaHS, where (–) BL representative; (–) Doubling NaOH concentration; (–) Doubling NaHS concentration; (–) Doubling both NaOH and NaHS concentrations. (2) Inducing

the Type 1 salts behaviour by varying the concentration of CO_3^{2-}, where (–) BL representative; (–) 25% of CO_3^{2-} reduction; (–) 50% of CO_3^{2-}reduction; (–) 75% of CO_3^{2-}reduction.

3.2. Continuous salt separation

Figure 2 presents the mass balances for the most promising experiments screened from HP-DSC analysis.

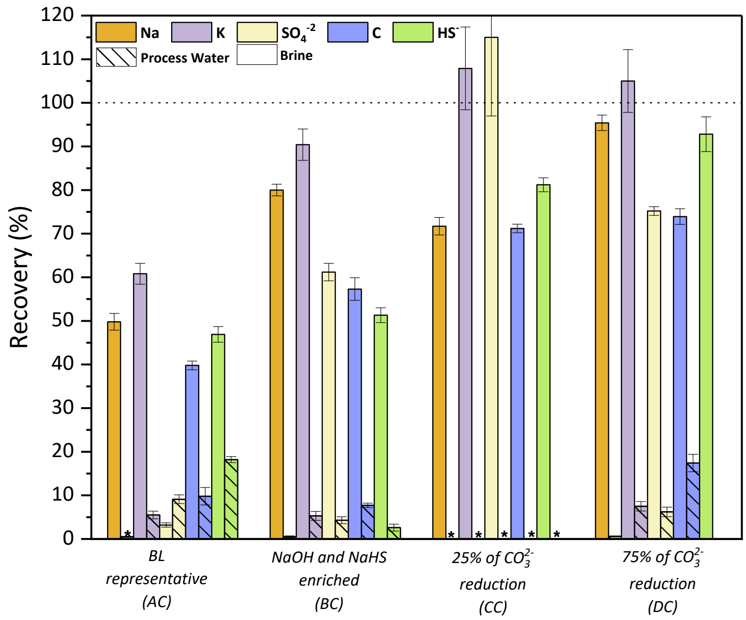

Figure 2. Recovery rates of sodium, potassium, sulphate, total carbon, and sulphide (S^{2-}) in the process water stream (hatched columns) and brine stream (filled columns).*Values lower than 1%.

The low recovery efficiency in experiment AC (overall salt recovery of 15%) indicates salts accumulation inside the vessel, which corroborates the behaviour found in Figure 1.1. As shown in Figure 2, both strategies adopted to induce a Type 1 salt behaviour to the model salt solutions seem to affect salt recovery efficiency positively. Reducing 75% of the carbonate concentration (Exp. DC) also resulted in higher salt recovery efficiency. It also indicates a low level of salt accumulation in the rig throughout the experiment since the mass balances are practically closed.

4. Conclusions

HP-DSC results showed that the salt solution used as reference model for black liquor exhibited Type 2 behaviour, with precipitation of insoluble salts at near-supercritical conditions. The strategy of increasing the concentration of the Type 1 salts, NaOH and NaSH, in order to yield global Type 1 behaviour proved to impact the temperature at which the salts precipitate, but did not prevent it. However, during continuous testing, the increase of both NaOH and NaSH concentration prevented the formation of a plug within the time frame of the experiment. An accumulation of salts in the vessel was observed, but this was linked to a suboptimal brine flow. The HP-DSC results indicated that both the inorganic exhibiting Type 1 behaviour after removing 75% of carbonate. Continuous salt extraction tests under supercritical water conditions were in line with the HP-DSC results and the mass balances obtained confirmed the efficiency of the removal of 75% of carbonate. The results obtained in this work showed that the two strategies to prevent or limit salt precipitation have been tested and validated, the carbonate removal proving to be the most reliable to prevent fouling in the separation vessel. These achievements will support the next steps to achieve the integration between salt separation and HTL for the valorisation of black liquor into biocrude in the H2020 project BL2F.