

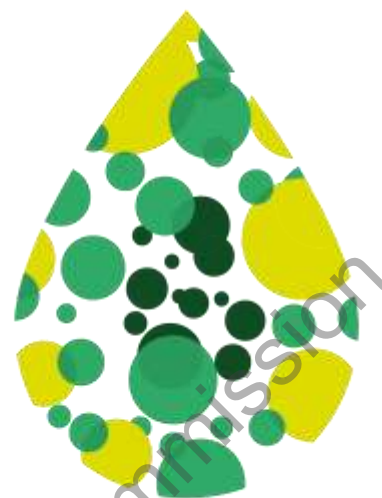
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Research and Innovation Action  
H2020-LC-SC3-2019-NZE-RES-CC

# D2.2 Report on integrated HTL- salt separation

**WP2 – Tasks 2.1 & 2.2**

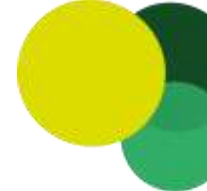
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## Abbreviations and acronyms

<b>SCW</b>	Super critical water
<b>SCWD</b>	Supercritical water desalination
<b>HTL</b>	Hydrothermal liquefaction
<b>WBL</b>	Weak black liquor
<b>VLE</b>	Vapour-liquid equilibrium
<b>VSE</b>	Fluid-solid equilibrium
<b>HP-DSC</b>	High pressure differential scanning calorimetry
<b>SNG</b>	Synthetic natural gas
$\dot{m}_{\text{Brine}}^{\text{ion}}$	mass flow rate of the ion in the brine
$\dot{m}_{\text{Desalinated stream}}^{\text{ion}}$	mass flow rate of the ion in the desalinated stream
$\dot{m}_{\text{Feed}}^{\text{ion}}$	mass flow rate of the ion in the feed
$\dot{n}_{\text{TOC}}^{\text{feed}}$	molar flow rate of total organic carbon in the feed
$\dot{n}_{\text{C in X}}^{\text{stream}}$	Carbon molar flow rate in compound X in either the brine or the desalinated stream
<b>ICP-OES</b>	Inductively coupled plasma optical emission spectroscopy
<b>TC</b>	Total carbon
<b>TOC</b>	Total organic carbon
<b>TIC</b>	Total inorganic carbon
<b>WP</b>	Work package
<b>ICP-OES</b>	Inductively coupled plasma – optical emission spectrometry
<b>DS</b>	Desalinated stream



## Executive Summary

The deliverable aims at bridging the gap between the HTL batch studies (D1.2), which studied the effect of various parameters on HTL products, and the work with the pilot plant for continuous HTL in WP1 (D1.3). The aim of the task is to study in details the salt separation in the presence of BL organic matter, the phase behavior of organic compounds, and to study the effect of process parameters and feed concentration on both salt separation and HTL. It follows up a first deliverable, D2.1, which covered the study of the phase behavior of inorganic salts present in BL and strategies to prevent fouling of the process, strategies on which this D2.2 is built on. This aims at bringing fundamentals understanding of the phase of key compounds in supercritical water while defining the parameters allowing optimal salt extraction while preserving HTL biocrude yield and quality.

The initial tasks in WP2 of the project identified two strategies for preventing fouling of the salt separator in black liquor (BL) processing: increasing NaOH and NaSH concentrations within acceptable ranges for Kraft processes, and partial causticization of BL, detailed in D2.1. Subsequent work (D2.2) aimed to study the phase behavior of BL inorganic and organic salts, confirming the efficacy of these strategies via continuous tests with sodium acetate, modeling various carboxylates found in BL. Phenolate, a significant salt category in BL, was also studied, revealing its efficient separation alongside inorganic salts and acetate, suggesting potential benefits for integrated processes.

Temperature is known to negatively impact HTL (D1.2), and it emerged as critical for both salt separation efficiency, with an ideal salt separation observed at 410-420°C, achieving up to 98% extraction. Tests with causticized BL demonstrated smooth operation without salt separator fouling, with the majority of organic matter separating into the brine along with inorganic salts, instead of the ending up in the desalinated steam. Brine flow emerged as critical for efficient processes, requiring at least 30% of feed flow to prevent salt accumulation. The yields of volatile monomeric compounds from continuous tests with diluted BL were comparable to batch tests (D1.2), indicating the viability of the latter results to estimate continuous processing outcomes.

Although most BL organics are separated along with inorganic salts, this approach offers advantages such as concentration of organics and salts in the brine, leaving over 60% of the BL feed with low salt and organic content. Moreover, the high temperatures required for salt separation do not adversely affect biocrude yields, as most organics are separated before reaching this zone. One option for optimizing HTL of BL include adjusting pH ahead of salt separation, with the associated risk of negatively impacting salt separation. The other option, with greater potential, is to embrace the natural phase behavior of BL organics, optimizing residence time and temperature in the brine extraction line to increase biocrude yield and quality. Both approaches would require further studies.

## Keywords

**Black liquor, Fuel, Aviation, Shipping, Hydrothermal liquefaction, Model substances, Sulfur, Product analysis, salt separation, supercritical water, biocrude, aromatic compound**



# 1. Introduction

The BL2F project aims to pioneer innovative technology for converting black liquor (BL) into fuel. Understanding how new technology work and optimizing it is pivotal. This report outlines the findings from the coupling of salt separation and HTL of BL, a byproduct of wood pulping. It is important to note that this report and the BL2F project specifically address BL sourced from Eucalyptus and do not encompass BL from alternative feedstocks like straw. The growing interest in hydrothermal liquefaction (HTL) of black liquor is acknowledged, with a comprehensive review of BL and BL-driven lignin conducted within the BL2F project by Lappalainen et al.(1)

Black liquor in its weak form prior to evaporation typically comprises approximately 10% organic and 5% inorganic content, predominantly salts like cooking chemicals. Understanding the phase equilibrium of salt mixtures is crucial for optimizing desalination streams and preventing equipment fouling due to the deposits of salt precipitates on the walls. Moreover, predicting the behavior of mixed salt compositions necessitates a systematic investigation under supercritical conditions for efficient salt separation. Initial studies conducted at PSI in late 2018 on a model salt mixture representative of black liquor revealed tendencies toward solid formation in the salt separator, hindering continuous mineral extraction. To address this problem of salt deposition, several potential strategies have been studied and two have showed their efficiency with model mixtures: increase of NaOH and NaSH concentration, and causticization, i.e. replacing carbonate by hydroxide (see D2.1).

In Task 2.2 of the project, integration of the salt separation with hydrothermal liquefaction of black liquor is studied at the Paul Scherrer Institute (PSI). The aim of the task is to go more in detail on the salt separation in the presence of BL organic matter and on the phase behavior of organic compounds in one hand, and to study the effect of process parameters on both salt separation and HTL. The overall process efficiency is also assessed, and its integration and operation constraints to a Kraft process is debated. The influence of temperature and residence time is investigated as well as the concentration of BL (dilution factor). This deliverable shows the procedure of the experiments, the following analysis steps and discusses the results.

## 2. Materials and methods

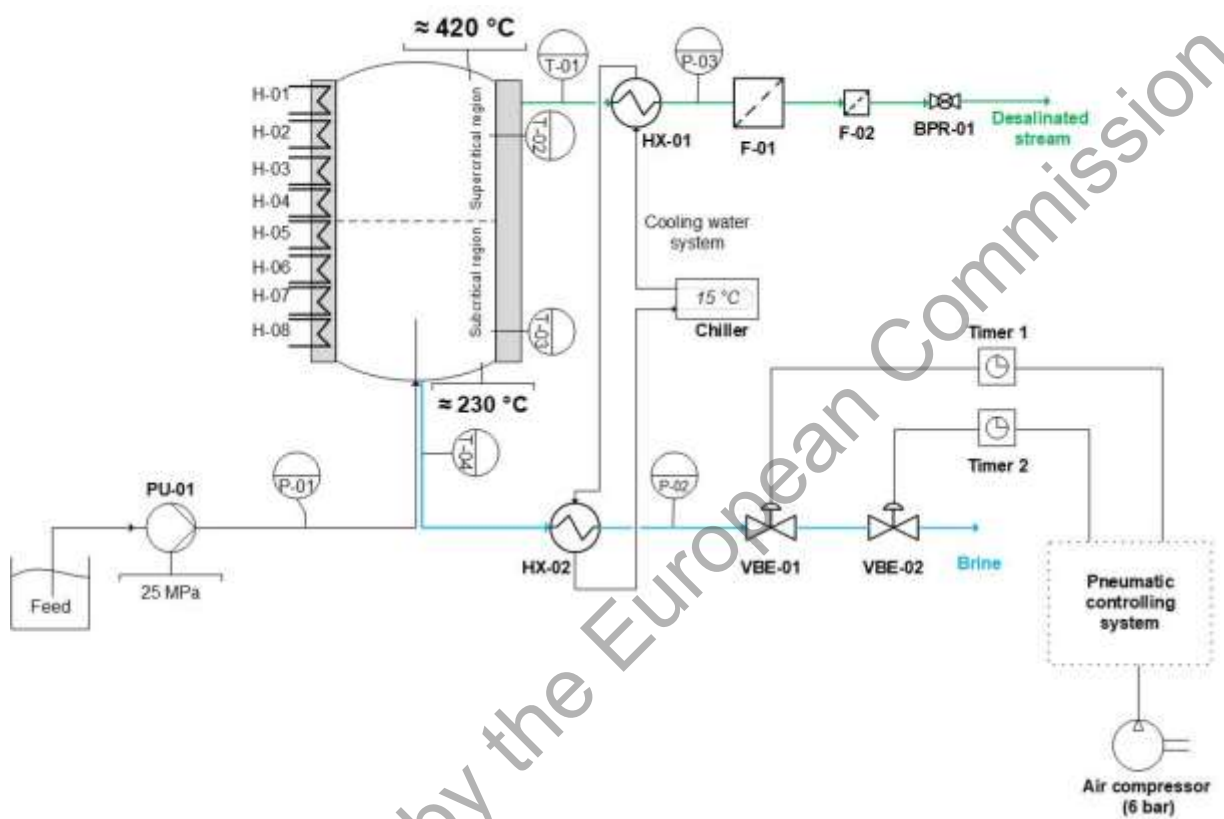
### 2.1. Salt separation tests

The salt separation tests were performed on the continuous salt separation test rig Salsan-II, already described in D2.1. In order to perform tests with heavy organic compounds typically present in black liquor, and to cope with solids present in the effluents (lignin precipitation, formation of coke), the test rig was updated. Figure 1 presents the modifications brought to the setup, which are mostly centered on a double pneumatic valve system for the semi-continuous extraction of the brine, instead of the mass flowmeter controller (Bronkhorst LIQUI-FLOW L29-ABD-11-z-80S coupled to a Bronkhorst EL-FLOW F-033C-LIU-11-K) initially used to regulate the brine mass flow rate. This way, the brine is extracted by successive small suction from the pressure decrease linked to the pressurization of the sampling volume.



Also, a large filter was added to the desalinated line to prevent blockage of the Tescom backpressure regulator mounted downstream of the cooler in the desalinated stream controls the pressure inside the vessel.

Finally, while most of the equipment (made of Zircaloy-2 or 316Ti SS) resisted the very harsh and corrosive conditions, a few thermocouples, most importantly T-02, were equipped with a pure titanium sheath to prevent the thermocouple from very fast corrosion.



**Figure 1 - Simplified flow scheme of the continuous salt separator Salsan II. PU-01: HPLC pump; BPR-01: backpressure regulator; F-01 and F-02: filters; MFC-01: mass flow controller; HX-01 and HX-02: heat exchangers; T-01, T-02, T-03 and T-04: thermocouples; P-01, P-02, and P-03: pressure indicators. The temperature indicated at the top and bottom are representative of the temperatures identified as ideal for salt separation.**

All the experiments were performed following the followed steps: (1) flush the setup at ambient temperature with DI water (generally overnight) until reaching the DI water conductivity value ( $< 5 \mu\text{S}\cdot\text{cm}^{-1}$ ); (2) pressurize the setup to set pressure of 250 bar; (3) heat up the fluids inside the separator to a subcritical water condition (150 °C); (4) setting the first four heaters to 450 °C, while the bottom four are set to 400 °C; (5) switch feed from water to the salt model solution to start the separation test ( $t = 0$ ); (6) flush the setup with DI water at the same conditions (pressure and temperature) and then proceed to subcritical conditions overnight (ca. 150 °C).



For the tests performed with BL, additional cleaning were performed. First, isopropanol was pumped in the setup to rinse a first time the unit. The coolers and the filters were separately cleaned with acetone to and the flushing solutions were collected for further analysis. Salt separation efficiency and the recovery of each element in each effluent were calculated by equations 1 and 2. Other terms and their equations are described and defined in the text.

$$\text{Total recovery} = \frac{\dot{m}_{\text{Brine}}^{\text{ion}} + \dot{m}_{\text{Desalinated stream}}^{\text{ion}}}{\dot{m}_{\text{Feed}}^{\text{ion}}} \cdot 100\% \quad (1)$$

$$\text{Recovery} = \frac{\dot{m}_{\text{Effluent x}}^{\text{ion}}}{\dot{m}_{\text{Feed}}^{\text{ion}}} \cdot 100\% \quad (2)$$

## 2.2. Feedstock

The black liquor utilized in our project was sourced from The Navigator Company's pulp mill in Portugal, maintained in its original state. It appears as a nearly uniform black liquid. Detailed information regarding its typical composition and properties can be found in Deliverable 1.1 (Feedstock Characterization), with key values provided in Table 1. To prevent oxidation, the feedstock was consistently stored in a refrigerator at 5°C in a closed vessel with the overhead purged with argon, as freezing it could potentially damage lignin molecules through mechanical destruction.

**Table 1 - Composition of Black Liquor from hard wood eucalyptus trees.**

Parameter	Unit		Value
pH			13.31
Conductivity	mS cm <sup>-1</sup>		75.50
Dry matter	wt.%	Slurry	14.50
Ash content	wt.%		4.92
Inorganic C	wt.%		0.18
Organic C	wt.%		4.59
Total C	wt.%		4.77
CO <sub>3</sub> <sup>2-</sup>	wt.%		6.48
Total S	wt.%		4.70
SO <sub>4</sub> <sup>2-</sup>	wt.%	Dry matter	1.88
HS <sup>-</sup>	wt.%		2.11
Total Na	wt.%		17.73
Total K	wt.%		1.28
Residual HO <sup>-</sup>	wt.%		5.35

## 2.3. Analytical methods

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectroblue SOP, Spectro Analytical Instruments) was used to analyse sodium, potassium and sulphur present in the samples. Volumetrically defined aliquots were weighed to determine the density, and then a large excess of H<sub>2</sub>O<sub>2</sub> was added to fully oxidize sulphides to SO<sub>4</sub><sup>2-</sup> and thereby remove the hazard of any H<sub>2</sub>S produced



during preparation of the samples for ICP analysis (the samples were acidified to 2.5 wt % nitric acid). For the samples containing organic compounds, aqua regia digestion was applied: around 0.25 g of the sample was treated with 1 mL of concentrated HNO<sub>3</sub> and 3 mL of concentrated HCl in PTFE vials and then heated in a microwave oven for 5 min at 500 W. Then, all the samples were filtered (0.45 µm) and diluted to a concentration between 1 and 100 mg L<sup>-1</sup> in PE volumetric flasks and stored in 5 mL PE falcon tubes until measurement. Calibration was done with standard solutions containing 1, 5, 10, 50, and 100 mg L<sup>-1</sup> of the elements of interest in the ICP-multi-element standard solution along with two blanks consisting of the DI water used in the tests acidified with the same amount of nitric acid.

Sulphide analysis was carried out by a UV-vis spectrophotometer (Macherey-Nagel, Nanocolor UV/Vis II). The specific Macherey-Nagel test kit for sulphide (NANOCOLOR test tube 985073), based on the methylene blue method, was used to measure all the samples. The difference between total sulphur and sulphide was used to determine the sulphate content in the model solutions.

Total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC) contents of BL samples were analysed using a TOC analyser (Dimatoc 2100, Dimatec Analysentechnik GmbH), and TIC was used to calculate the CO<sub>3</sub><sup>2-</sup> concentration. The samples diluted to the calibrated concentration range and maintained under stirring were injected into a quartz glass reactor where they were burnt at 850 °C under a constant oxygen carrier gas flow (200 mL min<sup>-1</sup>). CO<sub>2</sub> was detected with a non-dispersive infrared (NDIR) detector for determining the TC. For measuring the TIC, the samples were injected into a 10 wt. % solution of H<sub>3</sub>PO<sub>4</sub>, and the evolving CO<sub>2</sub> was stripped with the oxygen carrier gas flow and transported to the NDIR detector. Then, the TOC was obtained by subtracting the TIC from the TC. The analysis was repeated around seven times for each sample (standard deviation evaluation).

A second aliquot is used to determine and quantify aromatic monomers with gas chromatographs (GC). To qualify unknown components, Agilent's GC 6890N equipped with a non-polar capillary column (Rfxi-5Sil, Restek) and an Agilent 5973 MSD mass spectrometry detector is used (GC-MS). The underlying database originates from the National Institute of Standards and Technology (NIST). The quantification of the most important aromatic monomer compounds was done with an Agilent GC 7820A with a FID. The column inside the GC-FID is the same we use in the GC-MS setup. The procedure for sample preparation is based on the method used by Forchheim et al. [3]. The sample has to be placed in the correct matrix first to obtain the best possible results later. At first, the sample must be acidified to a pH around 3-4. We use concentrated hydrochloric acid in this step (20 wt. %, approx. 6M). The acidified liquid phase is then filtered again with a syringe filter (pore size 0.22 µm) to remove the precipitated components due to acidification. Afterwards 1,3 mL of the filtered sample is mixed with 0,52 mL of a prepared extractant in an Eppendorf tube. The used mixture contains mainly ethyl acetate, but also an internal standard (ISTD), pentadecane, which is needed later for quantification. The concentration of pentadecane is around 700 mg/L ethyl acetate. After mixing the sample and the extractant the tube is shaken for one minute and rested for a minimum of one hour. After the resting time is over, a clear phase separation is visible, in which the organic phase is the upper one. An aliquot of the organic phase is diluted in ethyl acetate (1:3 dilution) to get into the calibration range of the GC-FID. A total of ten different aromatic compounds can be quantified with our GC setup.



For each of them a distribution coefficient  $K_i$  for the used extraction procedure was determined, as described in D1.2.

Together with the dilution factor  $a$ , the extraction volume factor  $b$ , the ISTD factor  $c$  and the raw data  $\beta_{i,raw}$  of the GC-FID analysis following equation is given to determine the mass concentration of the compounds in the original samples.

$$\beta_i = \frac{\beta_{i,raw} * a * b * c}{K_i} \quad (3)$$

The dilution factor  $a$  describes the overall dilution of the original sample, the extraction volume factor  $b$  takes the ratio between the volume of the sample and the extractant into account and the ISTD factor  $c$  considers the ratio between the concentration of ISTD in the analyzed sample and the original ISTD concentration in the extractant.

To calculate the yields of the species  $Y_{i,BM}$  to increase the comparability between processes, we need the mass of the feedstock  $m_{feed}$  in the reactor before processing and the mass of the collected liquid product phase  $m_{liq,prod}$  as well as  $m_{tr,waf}$  and  $m_{total}$ .

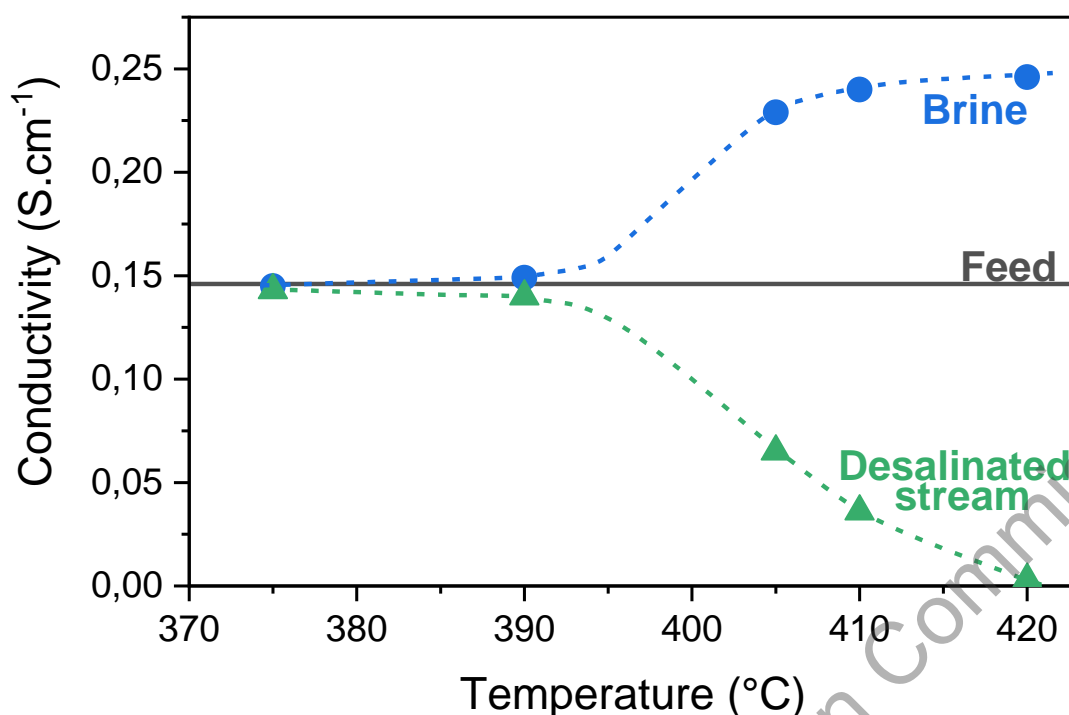
$$Y_{i,BM} = \frac{\frac{\beta_i}{\rho} * m_{liq,prod}}{\frac{m_{tr,waf}}{m_{total}} * m_{feed}} \quad (4)$$

### 3. Results and discussion

#### 3.1 Impact of temperature on salt separation

In WP1, the effect of temperature on biocrude yield was performed (D1.2) and indicated that the yield was decreasing significantly with increasing temperature, but also that short holding time were preferred. This is likely a direct effect of the high concentration of salts in BL. In order to be able to both separate salts and optimize the biocrude yield, a series of tests was performed with model salt solution to evaluate the effect of temperature on salt separation. The results are presented in Figure 2 and indicate that the conductivity, correlated to the concentration of salts, only starts to increase in the brine and decrease in the desalinated stream from ca. 395-400°C, and that the separation of the salts becomes truly efficient at ca. 420°C.





**Figure 2 – Evolution of the brine and desalinated stream conductivity with the temperature of the salt separator using the organic-rich model salt composition (see conditions of experiment GC’).**

An optimal salt separation at 420°C might lead into a reduced biocrude yield (according to the trends in D1.2) and greater coke formation (solid carbon). However, the low residence time of the continuous setup (hydraulic residence time of ca. 3 min) coupled with the salt separation from the main organic-rich stream, might counter-balance the lower yield expected by the high process temperature.

### 3.2 Phase behaviour of phenolate salt

The hydrothermal liquefaction of lignin yields among others to simple phenolic compounds (D1.2), as well as heavier/more complex polyaromatic compounds with phenol functions. These compounds, notably the heavy ones, are soluble in black liquor as a result of the high pH of the phenol functions, which present a (first) pKa in the 9-10 range (see Figure 3). One major unknown factor for an efficient iHTL of BL is the phase behavior of phenolics in supercritical water. Indeed, one could expect a phase separation of the phenolates salts, but some salts tend to react with water yielding their respective soluble base, like ammonium forming preferentially ammonia and hydroxide salt. This is caused by the drastic change of the properties of water, among other its dielectric constant, polarity and dissociation constant (i.e. pH scale). It can hence be that phenolic compounds (phenolates) precipitates along with the brine which would hinder the iHTL concept. To evaluate the phase behavior of phenolic compounds, tests were performed with phenol in a model salt solution with the updated test rig operated at 420°C.



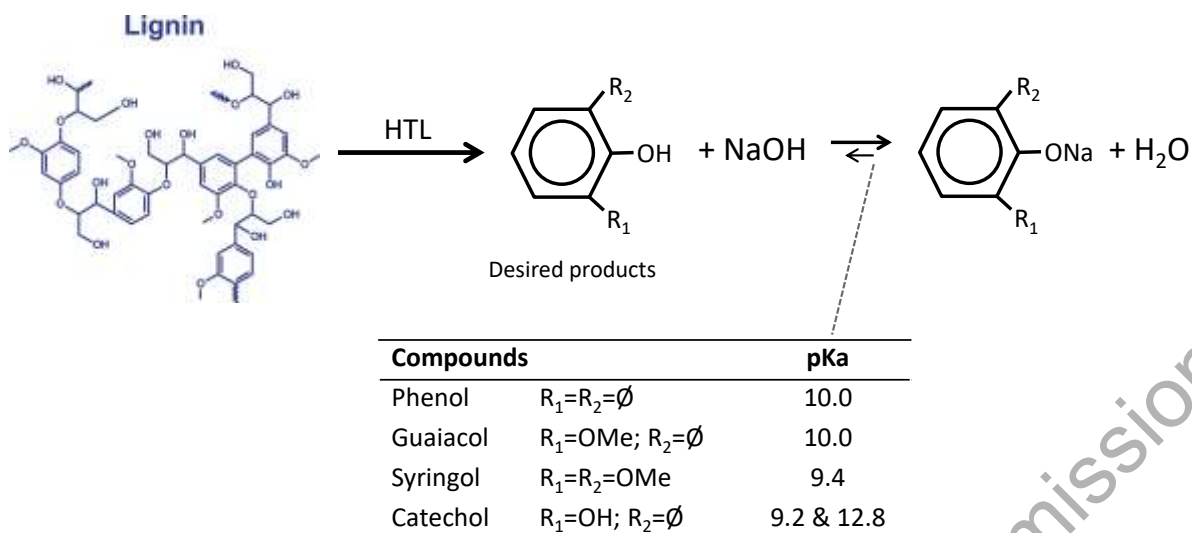


Figure 3 – Schematic presenting the acid-base equilibrium reaction of phenolic compounds, typical/desired products from lignin depolymerization, along with the pKa of several of these compounds.

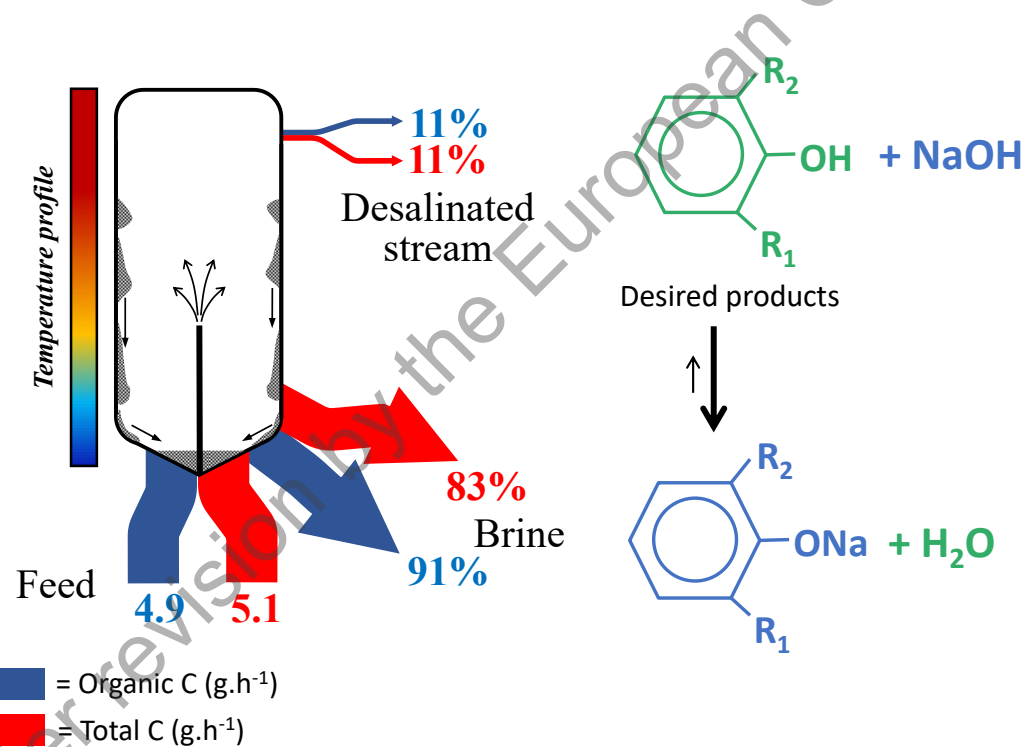


Figure 4 – Sankey diagram for the organic carbon and total carbon reached during the test with 0.5% phenol with acetate-containing model salt composition (see conditions of experiment DC) at 420°C (top of the salt separator). Note that phenol represents 30% of the organic carbon, the remaining 70% coming from acetate.



As it can be seen in Figure 4 and Table 2, mass balance of the total and organic compounds indicate that the presence of phenolate is largely favored over phenol and hydroxide. An important observation is that during the 5h test, at 0.5 wt% and 5 wt% phenol successively, no plug was formed indicating an overall type 1 phase behavior. As a result, most of the phenol, and the acetate, injected were recovered with the other salts from the bottom of the salt separator, in the brine. By extension, it can be expected that most other phenolates produced during the HTL and/or the lignin itself present in the black liquor would behave the same and separate from the main salt-depleted stream. However, if larger phenolic compounds, e.g. lignin, present the same phase behavior, this presents a risk of formation of solids which might plug the brine outlet.

This alters the initial objectives from the project which were to separate the salts from the main organic-rich & salt-depleted stream. However, this can also be seen as an opportunity as the main desalinated stream coming out of this process is now mostly salt-free and organic depleted, while the brine, which represents 30-35% of the inlet, contains all the organic compounds and salts. Aside of the production of biocrude, this can be seen as a mean to concentrate black liquor.

These results are in line with the observations made during iHTL of BL, in terms of pH of the desalinated stream (neutral), in terms of absence or a very limited presence of organic compounds / organic phase.

**Table 2 – Total mass and organic carbon mass balance, along with pH values during a test with 5% phenol with acetate-containing model salt composition (see conditions of experiment DC) at 420°C (top of the salt separator).**

Effluent	Total flow (g.min <sup>-1</sup> )	Total flow balance (%)	pH	Total carbon flow (mg.min <sup>-1</sup> )	Total C balance (%)	Organic carbon flow (mg.min <sup>-1</sup> )	Organic C balance (%)
Feed	6,3	-	12	85	-	82	-
Brine stream	2,2	35	12	78	91	70	83
Desalinated stream	3.8	61	7,3	9,1	11	9,1	11

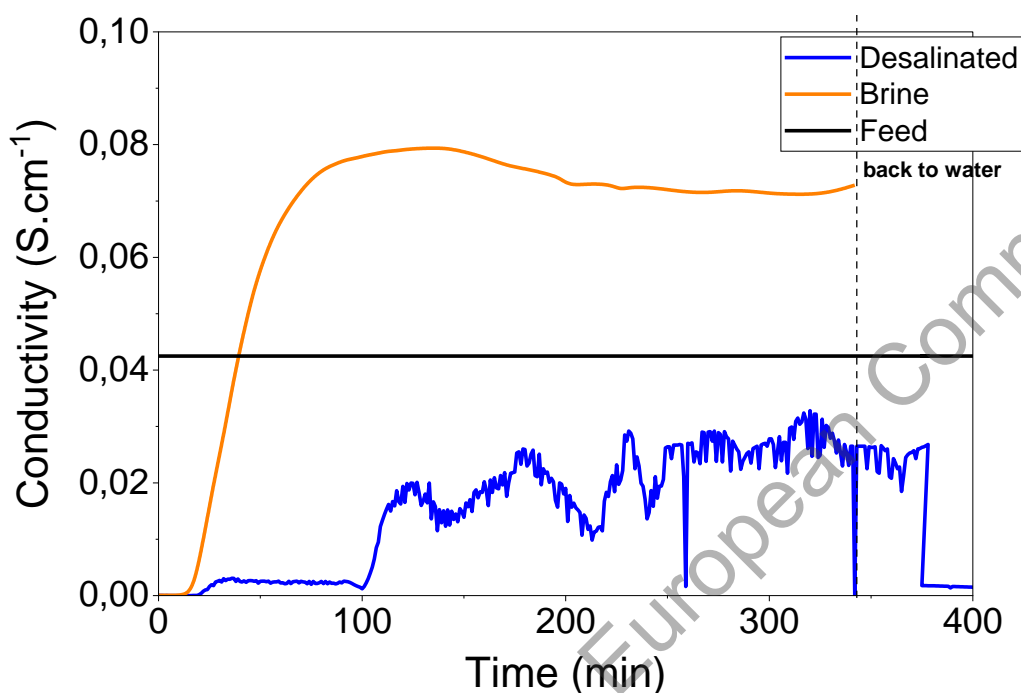
### 3.3 On the concomitant salt separation and HTL

A test was done with weak black liquor, from hard wood eucalyptus trees, received from the Navigator company. This is the reference black liquor settled for the project, with a representative analysis described in Deliverable 1.1. For the test, black liquor was diluted to 25% (1:4 dilution), adding salt to make up the inorganic content to 100% of BL. During this test, a plug formed inside the salt separator after about 2h, which is in line with the observations with the model salt solution.

Out of the two strategies identified to prevent fouling, it was decided to set the focus on causticization of the black liquor for its greater efficiency. A first test (BL2F\_BLD1) was done with BL diluted to 25%, inorganic salt content completed to 100%, with a carbonate to hydroxide ratio such that a causticization of 25% was reached. A plug was observed inside the reactor after a 4.2h. This proves



that causticization impacted salt deposition but did not prevent it in the presence of BL organics. What is also very likely is that during the treatment of the solution, organic compounds decarboxylated yielding carbonates (type 2 salts) adding up and favoring the precipitation of the salt mixture.



**Figure 5 - Evolution of the conductivity of the inlet and outlets during a iHTL test with 25% diluted BL with inorganic salt concentration supplemented to that of undiluted BL, with a 75% causticization (replacement of carbonates by hydroxides)**

Note that on the first attempt, a plug formed after 45min in the riser tube (inlet of the salt separator) due to the too small inner diameter the injection tube, dubbed riser tube. This was solved by making modifications in the setup allowing installing a tube with a larger inner diameter (lower resistance to pressure).

As it can be observed in Figure 5, a smooth operation was reached while feeding to our setup using 25% diluted BL with inorganic salt concentration supplemented to that of undiluted BL, with a 75% causticization. Neither plug was formed during this long test of ca. 6h, nor any rise of pressure, confirming that the strategy to prevent salt deposits accumulating on the walls of the separator work well with real BL. Note that the rise of conductivity of the desalinated stream after TOS 100min coincided with its change of color, a result of salts accumulated in the separation vessel overflowing from the top outlet. This can be prevented by maintaining a brine flow large enough, which was optimized in following tests.



Note that due to the small scale of the installation, notably the inner diameter of all the equipment, test with higher concentration of BL irrevocably led to a plugging and/or heavy organic deposit formation triggering very long cleanup and/or replacement of parts.

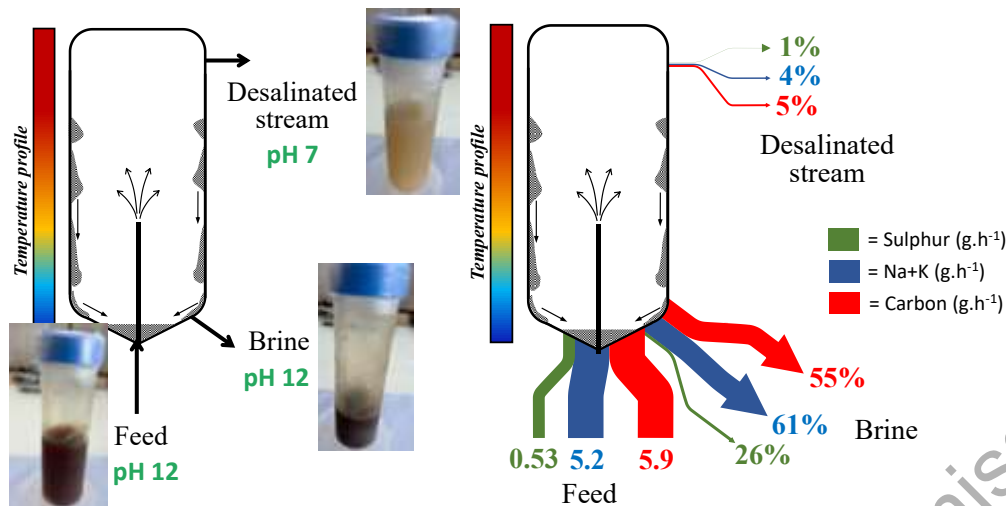
**Table 3 - Total mass and organic carbon mass balance, along with pH values during an iHTL test at 411°C (top of the salt separator) with 25% diluted BL, inorganic salts supplemented to undiluted BL with a 75% causticization. The deposits in the DS line are calculated on the hypothesis that they were steadily produced during the whole length of the test.**

Effluent	Total flow (g.min <sup>-1</sup> )	Total C flow (g.h <sup>-1</sup> )	Organic C flow (g.h <sup>-1</sup> )	S flow (g.h <sup>-1</sup> )	Na&K flow (g.h <sup>-1</sup> )	Biocrude (%C) <sup>a</sup>	pH
Feed	6,2	5,9	5,6	0,53	5,2	-	12
Brine stream	3,7	<0,05	<0,1	<0,005	0,22	29,4	12
Desalinated stream (DS)	2,3	3,2	3,0	0,14	3,1	1,6	7,0
Deposits in the DS line <sup>b</sup>	0,012	0,40	0,40	0,01	<0,05	0,1 <sup>b</sup>	N/A

<sup>a</sup> Based on the total carbon content measured by CHNS in the feed and biocrude extracted.

<sup>b</sup> Calculated using the biocrude composition from a run with 50% BL dilution (not enough deposits in the test at 25% for characterization)





**Figure 6 - Sankey diagram for sulphur, carbon and salts (cations Na & K) reached during the test with 25% diluted BL, inorganic salts supplemented to undiluted BL with a 75% causticization at 420°C (top of the salt separator).**

Figure 6 presents the sankey diagram for sulphur, carbon and salts (cations Na & K) reached during a repetition test of the one presented in Figure 5, performed with a higher brine flow (after optimization) and which was stopped after 3.5h. As it can be seen, the desalinated stream, that went through a zone heated at 420°C, was a light milky solution of pH 7, in phase with a low BL-based salt content. The brine produced was very dark, thicker and darker than the feed, and had the same pH as the feed (pH 12). The analysis of the streams (semi-)continuously collected during the steady state indicated that 61%, 55% and 26% of the salts (Na & K), total carbon and sulphur was collected in the brine, while only 4%, 5% and 1% could be found in the desalinated stream, respectively. Note that most of the carbon and sulphur collected in the desalinated stream were actually collected during in the deposited washed of the filter downstream the salt separator. The missing balances, 35%, 39% and 73% probably accumulated in the salt separator indicating that a higher brine flow, and/or a different design of the brine extraction line, to favor the flow of solid containing liquid, is needed to avoid accumulation over long period of time. Note that during the test performed at 50% dilution of black liquor, the carbon and sulphur balance could be closed but not the cations/ash (brine flow insufficient). The results with 50% dilution being quite similar to those with 25%, but the time for cleaning the setup significantly increased. For these reasons, and to lower the risk of plugging of the cold line, all the other tests were performed with 25% dilution.

A similar extraction as used in WP1 (e.g. D1.2) using ethyl acetate was used to extract biocrude from both the brine and the process water. As it can be seen in Table 3, the carbon-based yield of biocrude recovered in the desalinated stream was only 1.6wt%<sub>c</sub>, to which 0.1 wt%<sub>c</sub> of desposits could be added, while the biocrude yield in the brine was 29 wt%<sub>c</sub>. The low total yields can be linked to the low total C balance (ca. 65%) reached, which is linked to accumulation of carbon-containing salts in the salt separator.



Table 4 presents the composition of various biocrude produced from diluted BL conjointly with optimized salt separation. Overall, the desalination efficiency reached was comparable to that obtained with model salt solution. No significant different could be observed between the test at 25 and 50% BL dilution. The composition of the biocrude collected in the brine was overall in the 48-55% for C, 4.8-5.5% for H and 4.8-19% for S. These values are low in C and H and high in S when compared to the lignin present in the same black liquor (60, 5.7 and 2.6% respectively). This is also to compare with the C, H and S composition reached during batch tests performed without salt separation, which are in the range of 58-65%, 6,4-8% and 3,3-4,4% respectively. These observations could be explained by several phenomena: preferred extraction of lower quality (more O and S, i.e. more charges) biocrude and/or the reaction of the biocrude with the salts present at higher concentration in the brine.

The only biocrude-like sample present in the desalinated stream collected in quantities large enough to perform elemental analysis was collected during the cleaning of the large filter upstream the pressure regulator, and had a C, H and S composition of 44, 6,6 and 0,9%, respectively. These deposits might have either in the form of a solid suspension or an emulsion (biocrude droplets). As these organics went through the hottest part of the setup (above 400°C), a lower S content is expected and are in phase with the observations reported in D1.2. However, the particularly low C content indicates that the oxygen content must be rather high in this organic fraction.

A decrease of temperature, from 420°C to ca. 410°C, was systematically observed at the top of the SS when switching to phenol and salts or diluted BL mixed with salts. This was not observed when pure water or salts in water was fed in, and such observation cannot be explained yet. Indeed, one would expect that an endothermic reaction/physical-chemical would be the cause. Hydrothermal processes are generally endothermic at low temperatures but become exothermic at high temperatures, that is the temperature reached at the top of our salt separator,(2, 3) but hydrolysis, decarboxylation are endothermic reactions, as well as the degradation of guaiacol(4). Radical scission degradations reactions of lignin, favored at the conditions reached, could be exothermic.(4)



**Table 4 - Sampling time and composition of the biocrude collected during iHTL tests with 25% and 50% diluted BL, both with inorganic salts supplemented to undiluted BL with a 75% causticization.**

Feed & conditions	Temperature max <sup>a</sup> (°C)	Residence time <sup>b</sup> (min)	Stream	C (wt%)	H (wt%)	S (wt%)	Desalination efficiency (%) <sup>c</sup>	Yield (% <sub>c</sub> )
Lignin extracted from black liquor <sup>d</sup>	N/A	N/A	N/A	60,3	5,7	2,6	N/A	
	<b>411</b>	7	Brine	53,1	5,1	5,8	6,4	29,4
BL 25%, salt supplemented to undiluted BL, 75% causticization	<b>407</b>	9	Brine	52,2	5,1	12,7	-	16,3
	<b>402</b>	17	Brine	54,4	5,5	19,3	-	11,4
	413	<b>9</b> (half feed & brine flows)	Brine	48,5	4,8	4,8	5,5	13,2
BL 50%, salt supplemented to undiluted BL, 75% causticization	418	10	Brine	53,3	5,2	10,4	13,1	32,3
	413-418	N/A	Deposits from DS	43,8	6,6	0,94		1,4

<sup>a</sup> Top of the salt separator ; <sup>b</sup> Hydraulic residence time calculated using the measured brine flow, an average density of 0,6 cm<sup>3</sup>.g<sup>-1</sup>, an internal diameter of the reactor of 12mm and a length of the reactor of 222mm (half of the separator length) ; <sup>c</sup> Percentage of Na+K remaining in the desalinated stream (based on the feed inlet) ; <sup>d</sup> From D1.2



**Table 5 - Product yields (TOC-based) obtained during a few continuous test performed with diluted black liquor with salt supplemented to undiluted BL and with a 75% causticization. The yields are compared with those obtained in batch tests reported in D1.2.**

Parameters / Yield (mol% <sub>c</sub> <sup>a</sup> )	Batch test BL (D1.2)	BL 25%, salt supplemented, 75% causticization	BL 50%, salt supplemented, 75% causticization	Batch test BL (D1.2)	BL 25%, salt supplemented, 75% causticization	BL 50%, salt supplemented, 75% causticization
Temperature (°C)	400	407 <sup>b</sup>	418 <sup>b</sup>	375	230-407 <sup>c</sup>	230-418 <sup>c</sup>
Residence time <sup>d</sup> (min)	20	5	4	5	9	10
Stream	Batch <sup>e</sup>	Desalinated stream	Desalinated stream	Batch <sup>e</sup>	Brine	Brine
2-Methyl-Cyclopentanone	0,05	0,15	0,15	0,02	<LoQ	<LoQ
Phenol	0,05	0,12	0,14	0,04	<LoQ	0,01
o-Cresol	0,02	0,07	0,12	0,02	<LoQ	0,01
Guaiacol	<LoQ	0,05	0,08	0,01	0,15	0,07
Catechol	0,06	0,09	0,10	0,27	0,09	0,08
3-Methoxycatechol	<LoQ	<LoQ	<LoQ	<LoQ	0,09	0,04
3-Methylcatechol	0,10	0,09	0,06	0,28	0,04	0,02
4-Methylcatechol	0,10	0,08	0,03	0,60	0,05	0,03
Syringol	<LoQ	0,02	<LoQ	<LoQ	0,41	0,14
4-Ethylcatechol	0,04	<LoQ	<LoQ	0,25	0,03	0,02
Vanillin	<LoQ	<LoQ	<LoQ	<LoQ	0,03	<LoQ
Syringaldehyde	<LoQ	<LoQ	<LoQ	0,05	<LoQ	<LoQ
Acetosyringone	<LoQ	<LoQ	<LoQ	0,01	<LoQ	<LoQ
<b>Sum</b>	<b>0,42</b>	<b>0,68</b>	<b>0,68</b>	<b>1,55</b>	<b>0,89</b>	<b>0,40</b>
Molar TOC fraction	0,6	2,5	5,0	2,2	6,6	6,2

<sup>a</sup> The yield of the compound X is calculated as follow:  $Y_X = 100 \times \dot{n}_{C\ in\ X}^{stream} / \dot{n}_{TOC}^{feed}$ ; <sup>b</sup> At the top of the salt separator; <sup>c</sup> Gradient of temperature in the salt separator. The temperature the organic matter in the brine has been exposed to cannot be determined; <sup>d</sup> Hydraulic residence time calculated. Brine calculated using the measured brine flow, an average density of 0,6 cm<sup>3</sup>.g<sup>-1</sup>, an internal diameter of the reactor of 12mm and a length of the reactor of 222mm (half of the separator length); Desalinated stream: DS flow, density of 0,45 cm<sup>3</sup>.g<sup>-1</sup>, reactor length of 444mm; <sup>e</sup> No salt separation



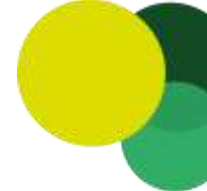


Table 5 presents the yields of calibrated volatile monomeric compounds obtained during a various continuous tests performed with diluted black liquor and are compared with those obtained in batch tests reported in D1.2. Overall, only syringol is found in a yield significantly higher in the brine when compared to DS stream, while the lightest compounds, i.e. 2-Methyl-Cyclopentanone, phenol and cresols, are found in yields significantly higher in the DS.

All these compounds account for a rather large proportion of the total organic carbon found in their respective stream, both for brines (6-7%) and desalinated streams (3-5%). These values are overall could however be explained by the different residence time and temperature, both decreasing the monomeric product yields when increasing.

The sum of all calibrated volatile monomeric compounds are in the same order of magnitude to these obtained from the bath tests reported in D1.2. It should be noted though that the longer storage time prior analysis for the samples from the continuous tests might have impacted the concentration of the compounds (condensation reactions). Similar yields were reached in both the desalinated stream and the brine. Note that this is not necessarily in contradiction with the results presented in Figure 4, as the light phenolic compounds observed in the DS stream could have been formed as the stream went through the hottest part of the separation vessel.

### **3.4 Strategies to prevent salt precipitation and the integration of iHTL within a Kraft plant: evaluating the pros and cons and perspective of development**

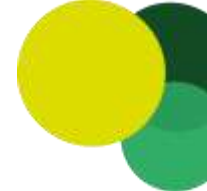
As explained earlier in this document, two strategies have been identified to prevent clogging of the salt separator by the salts present in black liquor. In order to integrate an HTL unit equipped with a supercritical water salt separation system, several aspects have to be taken into account and are discussed in this section.

When causticization of weak black liquor (BL) is considered, several aspects linked to scaling up of the process and integration :

- The work done in this task allow reaching the desired causticization level but require extensive solid separation. Scaling up the filtration/separation of  $\text{CaCO}_3$  from BL might a concern for experts in Kraft process (Valmet), and justify further studies on a scalable causticization procedure of BL.
- An alternative approach of separating the (small)  $\text{CaCO}_3/\text{CaO}$  particles from BL is to co-feed them to the HTL/salt separation unit. This may reduce the risk of fouling, similar to how activated carbon (AC) is expected to function as nucleation sites. Experts in Kraft process (Valmet) finds the addition of small amount of  $\text{CaCO}_3$  (<10% of BL dry matter) to the boiler acceptable.

In WP4, it was considered that 30% would be extracted from the Kraft process to go to HTL. If 50% of the causticization from this 30% is utilized, or a 50% increase of NaOH and NaSH concentrations, and the brine is fed back in the kraft process upstream the boiler, several risks arise:





- NaOH may lead to an increased corrosion at the colder parts of the evaporator and boiler, necessitating the use of alternative steels (more carbon steel and less stainless steel). Notably, in some plants where NaOH is used at higher concentrations (such as in Brazil), significant corrosion has been observed. There are no immediate solutions to this issue other than investments in infrastructure (upgrades) or risking an accelerated aging of the plant.
- An increased carryover of salts in the boiler will lead to more ash and consequently more fouling. The NaOH in black liquor may be converted to  $\text{Na}_2\text{CO}_3$  during combustion of BL in the recovery boiler furnace which will favor fouling. If fouling occurs on parts that cannot be continuously cleaned, it may necessitate stopping the boilers, incurring significant operational costs.

Regarding the strategy consisting in increasing the sulfide and/or hydroxide, it is important to note that the causticizing plant often limits/defines the salt concentrations and that the concentration of Na & S added to wood is determined by wood quality, wood wetness, and type, so the NaOH and NaSH concentration cannot necessarily easily be adjusted within Kraft process. As for sulfide specifically, increasing its content within the weak black liquor prior HTL & salt separation, and reinjecting the brine to the boiler will bring the system closer to white liquor concentrations, potentially requiring the selection of other materials for the boiler. Also, increasing sulfur content in wood (sulfidity) is not detrimental to the process but can add costs to remove the smell associated with sulfur compounds produced.

The total need for NaOH is typically 350 kg/air dry ton of pulp, most of which is recycled within the process. To compensate for losses, NaOH is added somewhere in the kraft process to maintain a constant Na concentration. This could be done before HTL to prevent fouling. In new mills, the recovery of salts in the kraft loop is typically 99.9%, requiring approximately 5-10 kg of NaOH/air dry ton of pulp to cover the losses. In old mills, where the recovery of salts in the kraft loop is typically 99% or down to 98%, approximately 25-30 kg of NaOH/air dry ton of pulp are typically added. This approach limits the need for causticization and its negative impact on the lime kiln, which is the most costly part of a kraft process.

A solution to the problems/points of worry described above is not to reinject entirely the brine, thereby extracting some Na & S from the Kraft process loop. These extracted components would need to be injected elsewhere in the process to maintain a constant quantity of Na & S. This injection can be done before HTL to take advantage of salt addition (if type 1, such as NaOH and NaSH). The additional expenses incurred due to waste treatment and the cost of injected salts would be offset by the production of more valuable biocrude obtained through HTL, as well as the energy savings from eliminating the need to evaporate water.

In summary, achieving a harmonious balance among all expenses is crucial. The addition of NaOH to weak black liquor (BL) prior to hydrothermal liquefaction (HTL) presents a favorable choice as it is a necessary step regardless, does not entail any direct additional expenses before HTL, and could potentially prevent fouling if the quantity of NaOH added is adequate. However, this option is more suitable for older, less efficient plants. Causticization could still be a viable alternative provided that measures are taken to control and mitigate the effects of corrosion and fouling to a reasonable extent. To assess reasonability, several factors need to be taken into consideration, including the proportion of weak BL allocated for HTL, the extent of causticization (increases downstream corrosion), and the

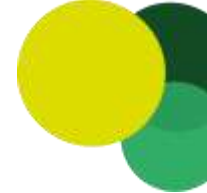




percentage of NaOH converted back to  $\text{Na}_2\text{CO}_3$  during HTL (decreases downstream corrosion). Conversely, incorporating NaSH may not be prudent due to the supplementary costs associated with gas cleaning.

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## 4. Summary and perspectives

In the two first tasks from WP2, two strategies to prevent fouling of the salt separator by the salts present in BL have been identified: increase of both NaOH and NaSH concentration, within a concentration range acceptable for Kraft process, and the partial causticization of the BL. This was described in detail in D2.1. The following up work described in this deliverable aimed first at studying the phase behavior of BL inorganic salts together with organic salts, as well as evaluating the validity of the two strategies to prevent fouling. Continuous tests with sodium acetate, a stable organic anion used to model the various carboxylates present in the BL, allowed to confirm the efficiency of the two strategies, with smooth and efficiency salt separation observed for at least 6h operation. The use of these strategies in a salt separation-HTL process integrated in a Kraft process would be possible but under certain constraints. These constraints should be defined after a careful evaluation of the risks (e.g. faster corrosion/fouling in the boiler) and the benefits associated.

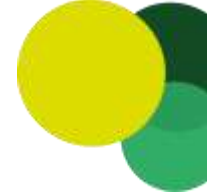
Another category of salts found in black liquor are phenolates, mostly lignin (poly-phenolic compounds) and mono- or oligomeric phenolic units produced from the liquefaction of the lignin. The effect of these salts on the salt separation efficiency, using phenol as model compounds, was also studied with a causticized model black liquor and allowed to confirm that phenolate does separate very efficiency along with the inorganic salts and acetate. These observations rule out the formation of phenol and NaOH (the corresponding acid) over phenolate and water, which can reasonably be extended to all other phenolic compounds. A positive outcome is that phenolate does not impact the efficiency of salt separation and allowed smooth operation even at high concentration (lignin concentration range)

The first step in the optimization of the concomitant salt separation and HTL from black liquor (BL) was to evaluate the effect of temperature on the salt extraction efficiency. Temperature was identified as critical for salt separation, as for the efficiency of HTL: the higher the temperature, the better is the salt separation, while the lower it is, the lower are liquid organic yields. It was found that an optimal salt separation was reached at around 420°C with an extraction up to 98%, yielding desalinated stream with a pH of 7, while the feed had a pH above 13.

The various tests performed with causticized black liquor proved to allow rather smooth operation with the absence of fouling of the salt separator, proving once more the efficiency of causticization to prevent it. The majority of the organic matter was found to separate from the mainstream in the salt separator, and ended up in the brine along with the inorganic salts. These results are in line with the ones main with phenolate and acetate. The brine flow was found to be critical in a smooth and efficient process and needs to be rather at least higher than 30% of the feed flow to prevent accumulation of salts in the salt separator. The yield of biocrude obtained in the brine were found to be up to 30%<sub>c</sub>, while for the one in the desalinated stream was typically below 2%<sub>c</sub>. The composition of that biocrude collected in the brine shows a lower quality than these obtained in batch tests (D1.2), notably for its sulfur content with was typically in the 5-10% range.

The yields of volatile monomeric compounds obtained in various continuous tests with diluted black liquor are comparable to those from batch tests and constitute a sizable proportion of the total organic carbon in the brine (and in the desalinated stream). Syringol was found to be significantly higher in yield in the brine than in the desalinated stream, while lighter compounds like 2-Methyl-





Cyclopentanone, phenol, and cresols are significantly higher in the desalinated stream. Despite differences in residence time and temperature impacting yields, overall yields are comparable to batch tests indicating that the trend observed in bath mode would apply to a continuous process, with similar yields in both the desalinated stream and brine.

Overall, the proof of concept of integrating salt separation to HTL is passed, but due to the nature of the organics in BL, most organics are separated from the mainstream along with the inorganics salts. While different from the intended concept, this brings some interesting outcomes, such as a concentration of organics and salts in the brine, leaving more than 60% of the BL fed with very low salt and low organic content. Another advantage is that the high temperature required to reach a deep salt separation, which should negatively affect the yield in biocrude, will not be detrimental to the biocrude yield (e.g. important gas formation). Indeed, most BL organics are separated from the mainstream before they reach this high temperature zone (or will quickly leave by gravity).

Two options exist for and a follow up work to optimize an HTL of BL:

- With the idea to reach the initial intention of the project, the pH could be adjusted ahead of the salt separation, e.g. by cofeeding CO<sub>2</sub>, which might positively impact the phase behavior of phenolic compounds and maybe also carboxylates. This would however trigger a new salt separation optimization, and potentially a whole new study as the phase of the salt mixture likely will negatively be affected, i.e. salt precipitation due to the addition of carbonates.
- With the idea to embrace the natural phase behavior of salts and organics from BL in supercritical water, one could apply a salt separation as described in this deliverable, followed by a brine outlet being maintained at an adequate HTL temperature. This would allow organics to be exposed to optimal HTL conditions for a given residence time, prior to cooling down and depressurizing the stream. This would allow to separate the salts and most organics from the mainstream while further optimizing the biocrude yield.

These options represent interesting prospects for continuing the project and its concept, which are believed to be very promising for HTL. However, many challenges are still ahead of a possible commercial application with such challenging effluent that is black liquor.

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