BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D1.1 - Report on the Feedstock Characterization

WP1 - Task 1.1

30th September 2020 [M6]

Lead Beneficiary: Valmet

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Disclaimer

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Grant Agreement n°884111.

Document Information

Grant agreement	884111
Project title	Black Liquor to Fuel by Efficient Hydrothermal Application integrated to Pulp Mill
Project acronym	BL2F
Project coordinator	Prof. Dr. Tero Joronen
Project duration	1st April 2020 – 30th November 2023 (36 Months)
Related work package	WP 1 – HTL-oil production
Related task(s)	Task 1.1 - Feedstock
Lead organisation	Valmet
Contributing partner(s)	PSI, KIT, NVG, Valmet
Due date	30th September 2020
Submission date	30th September 2020
Dissemination level	Public

History

Date	Version	Submitted by	Reviewed by	Comments
30th September 2020	N°1	Tero Joronen	David Baudoin, Maximilian Wörner	

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Abbreviations and acronyms

Acronym	Description
AES	Atomic Emission Spectroscopy
AOX	Adsorbable Organic halides
BL	Black Liquor
BL2F	Black Liquor to Fuel project
CHNS	Elemental analysis of Carbon, Hydrogen, Nitrogen and Sulphur
COD	Chemical Oxygen Demand
DAD	Diode Array Detector
DM	Dry Matter
DMSO	Dimethyl Sulfoxide
EDX	Energy-Dispersive X-ray spectroscopy
GC-FID/MS	- Gas Chromatography (GC) with Flame Ionization Detector (FID) and Mass Spectrometry (MS)
GPC	Gel Permeation Chromatography
HTL	hydrothermal liquefaction
ICP	Inductively Coupled Plasma
ICP-AES	- Inductively Coupled Plasma - Atomic Emission Spectroscopy
KIT	Karlsruhe Institute of Technology, a partner
NDIR	Non-Dispersive Infrared
NVG	The Navigator Company, partner of BL2F project
PDI	Polydiversity Index
PE	Polyethylene
PP	Polypropylene
PSI	Paul Scherrer Institute (Switzerland), a partner

RB	Recovery Boiler
SEM	Scanning Electron Microscope
SEC	Size Exclusion Chromatography
TAU	Tampere University, the coordination partner
TC	Total Carbon content
TGA	Thermal Gravimetric Analysis
TIC	Total Inorganic Carbon content
TOC	Total Organic Carbon content
TX	Total amount of halides
UV	Ultraviolet (light)
VOC	Volatile Organic Compounds
XRF	X-Ray Fluorescence

Executive Summary

Valmet coordinated the delivery of sufficient quantities of BL from NVG’s pulp mill to project partners for chemical and physical analyses. KIT and PSI analysed the composition and properties of black methods as follows: elementary analysis, ash content, heating values, XRF/ICP as well as GPC. Analytical results are shared in this document. The results are well in line with the findings of literature. The different methods are compared and further standardized is required.

Keywords

Black liquor, Chemical properties, Physical properties

1 Introduction

The BL2F project aims for developing novel technology for converting black liquor (BL) to fuel. As in any conversion process, knowing the quality of the feedstock is in key role. This report describes the results of characterization of BL. BL is a side stream of pulping of wood. The two main sources of pulp are soft wood (mainly spruce and pine) and hard wood (eucalyptus and birch). The selected primary feedstock in the BL2F project is BL from Kraft pulping of Eucalyptus. This report and the BL2F project do not handle BL from other feedstock, such as straw.

The HTL of black liquor has gained increasing interest in the scientific community. A review of the BL and BL driven lignin is made in the BL2F project by Lappalainen et al. (Lappalainen et al. 2020).

The feedstock collection and transport coordinated by Valmet and done by the Navigator Company. Valmet is the responsible partner of this deliverable. The BL analyses in this document were made in Paul Scherrer Institute (PSI) at Switzerland, and in Karlsruhe Institute of Technology (KIT) at Germany.

Black Liquor

Black Liquor is a general name for side-stream of pulping, that contains most of the hemicellulose-based components and the lignin of the wood, Additionally, BL contains the cooking chemicals. In the chemical pulping, the main added chemical is NaOH (sodium hydroxide), but especially in Kraft pulping, some sodium sulfide (Na_2S) is applied in dissolving lignin from the fibers. In cooking, hemicellulose is decomposed to sugars and acids. The cooking chemicals, that are very basic, soften the lignin and make it soluble to water. Thus, BL normally contains about 95 % of water after the washing phase of pulp. The chemical composition of BL depends on the processed raw material. BL is a very complex aqueous solution, composing of different organic materials and mainly soluble salt ions (Cardoso et al. 2009). The cooking chemicals are recovered typically in a recovery boiler (RB), where the BL with elevated solids concentration is sprayed. In the RB, the sodium sulfate (Na2SO4) reduces back to the cooking chemical sodium sulfide. In the evaporation and recovery stages, several additive materials can be added to black liquor. For instance, soap, biosludge, sawdust can be applied (Zhao et al. 2016). In this report, we will handle only BL that has not had any added material.

The typical elements of the BL are presented in the Table 1. below. This document handles only the BL for Kraft process. In the soda process, solely sodium hydroxide is applied for dissolving the pulp.

Table 1. Results from the elementary analysis of different black liquors. Elementary composition (% mass per dry solids) (Cardoso et al. 2009).

Liquor (type of processed wood)	**Mill location**	**C**	**H**	**N**	**Na**	**K**	**S**	**Cl**	**Si**
Hardwood/Eucalyptus grandis	Brazil/mill A (Kraft process)	30.8	3.6	0.01	21.8	1.8	3.7	4.5	0.1
Hardwood/E. grandis	Brazil/mill B (Kraft process)	35.2	3.7	–	21.2	2.1	3.0	4.3	–
Hardwood/E. grandis	Brazil/mill C (Kraft process)	29.6	3.6	–	18.7	2.2	4.4	2.6	–
Hardwood/E. grandis	Brazil/mill D (Kraft process)	34.8	3.4	0.04	18.3	2.1	3.6	3.2	–
Hardwood/E. grandis	Brazil/mill E (Kraft process)	32.3 ±0.3	3.1 ±0.1	0.04 ±0.01	23.5 ±3.2	1.8 ±0.3	4.9 ±0.5	2.2 ±0.3	–
Fibrous plant/Bambasa vulgarisa	Brazil/mill F (soda process)	35.4	3.6	0.30	19.3	3.3	0.2	1.3	3.8
Softwood/Pinus sylvestris and Pinus caribaeab	Scandinavia and North America (Kraft Process)	33.9 to 35.8	3.3 to 3.6	0.06 to 0.07	17.2 to 19.8	1.4 to 2.2	4.6 to 5.7	0.3 to 0.9	–
Hardwood	Scandinavia (Kraft process)	33.2	3.3	0.08	20.8	2.6	5.2	0.3	–
Hardwood/Eucalyptus	North America (Kraft process)	37.3	3.6	0.09	17.3	1.8	3.4	1.6	–
Fibrous plant/Straw	South America (soda process)	39.1	4.5	1.0	8.8	4.1	0.8	3.5	0.23

2 Feedstock selection & storage

The BL analyzed in this document was received from the Navigator company. It originates from Eucalyptus. The sample collection was made after the first phase of the evaporator. The target solid content of the BL was 10 - 20 %. This is the concentration that we, at the moment, consider to be the BL extracted to the HTL process. The water content is slightly decreased at this phase in evaporation, compared the BL received from the washing.

The storage of BL was identical for PSI and KIT. The samples were collected at the same moment. The BL was stored in big bottles in the fridge around 3-8 °C. Freezing must be avoided because it can lead to phase separation and structural changes of the macromolecules. Every time after opening the bottle it should be purged with inert gas. Otherwise contact with oxygen from the air will lead to oxidation of some compounds, e.g. sulfide. For better handling, up to 200 mL of the BL is filled in smaller air-tight polyethlyene or polypropylene flasks. It also avoids the regular opening of the large bottle and associated risk of oxidation.

3 Analysis methods

The black liquor was characterized using a variety of analytical methods to determine the elemental composition, physical properties and energy of content. Not all methods could be applied for the pristine black liquor, therefore it was dried at 105 °C for 24 h in a furnace and dry matter recorded. The results of the pristine black liquor and dry matter are listed in individual tables. The methods used to characterize the pristine black liquor and dry matter are described below.

Viscosity and Density:

The viscosity of the pristine black liquor was measured on a rheometer (Anton Paar, model MCR102) at 20 °C and 50 °C with a cylinder spindle. The shear rate and the rotation speed were constant over the entire procedure. The density of the liquid was obtained with an Anton Paar densitometer (model DMA 4500M) at 20 °C.

pH-conductivity

The pH measurements were performed on a pH-meter (SCHOTT®, Handylab pH/LF12). The pH-meter was calibrated prior to measurements with the use of a buffer solution (pH 7) at 25 °C.

Conductivity measurements were performed using the SCHOTT®, Handylab pH/LF12 conductivity meter at room temperature. The calibration of the conductivity meter was performed prior to measurements with the use of 0.1 M KCl solution provided by the manufacturer.

TX/AOX

Halide content was analyzed with a pyrolysis microcoulometer (Behr Cl 10). Organic and inorganic content of all halides in the black liquor were measured separately. The total amount of halides (TX), and organic halides (AOX) were obtained from 10-20 mg of the pristine black liquor sample for coulometric analysis. For the organic fraction 100 mL of an aqueous solution, including 0.1 or 0.2 mL of pristine BL and deionized water was produced. The solution was mixed with a defined amount of activated carbon. After one hour of shaking, the solution was filtered to remove the aqueous phase. The solid residue was washed to remove all of the inorganic compounds sticking to the activated carbon. Afterwards the organic halide content was measured in the same microcoulometer by burning the activated carbon.

Total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC) analysis

At PSI the TC, TOC, and TIC of liquid samples were analyzed on a TOC analyzer (Dimatoc). The samples were diluted with deionized water to the calibrated concentration range and injected into a quartz glass reactor where they were burnt at 850 °C under a constant flow of oxygen carrier gas (200 mL min^{-1}). CO_2 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_3PO_4 and the evolving CO_2 was stripped with the oxygen carrier gas flow and transported to the NDIR detector. The TOC was obtained by subtracting the TIC from the TC. The analysis was repeated around 6 times for each sample and standard deviation evaluation calculated.

At KIT a similar device and procedure was used for TC analysis. The same method was used for both TC and TIC analysis. TOC was calculated by subtracting TIC from the TC value.

Dry matter content

At PSI the dry matter of the black liquor was determined by heating a sample (10-20 g) at 105 °C in open-air until no further evolution of weight was detected (within 4 hours).

At KIT the solid content was determined with a moisture analyzer (Satorius MA 150). The sample was heated up to 105 °C until a constant moisture value was reached (100% - moisture content = dry solid content). After approximately four hours, the device showed a constant value of moisture content.

Carbon, hydrogen, nitrogen, and sulfur elemental analysis (CHNS)

At PSI CHNS analyses were performed on an elemental analyser (Vario EL cube, Elementar). Liquid samples (25-50 mg) and solid (5-8 mg) samples were burned at 1150 °C in a quartz glass reactor with the aid of a WO_3 catalyst. In a second quartz glass reactor, NO_x species were reduced to N_2 by a Cu catalyst. Carbon is detected as CO_2 and nitrogen as N_2 with a TCD detector, while sulphur is detected as SO_2 with an IR detector. Sulfanilamide was used as standard sample to determine the daily factor (theoretical content/actual content). For the analysis of hydrogen in dry solids, the water trap is removed. Measurements were performed at least 5 times for each sample (standard deviation evaluation).

At KIT the CHNS analyses were carried out using the same method and equipment as in PSI, however, the samples were dried for 24 h prior and stored in a desiccator.

ICP-AES analysis

ICP-AES analysis was performed on an Agilent ICP-AES 725 analyzer, in order to quantify elements that could not be analyzed by CHNS analysis, which include cations in acidic aqueous solutions. Inside the ICP a plasma is generated out of Argon with high frequency electromagnetic field (40 MHz, 2 KW). The compounds of the sample are taken apart in their atomic components and ionized, which make them detectable for AES. For the ICP preparation, the samples (20-30 mg) were digested with aqua regia (30% conc. hydrochloric acid and 65% conc. nitric acid, ratio 1:3) in a microwave oven (Anton Paar Multiwave 3000) for 2 hours. The samples were taken from the same stock of dried black liquor like the samples for the CHNS analysis.

XRF and SEM-EDX

Further analysis of the dry matter was done by a XRF spectroscopy (Bruker Pioneer S4), and SEM pictures taken including an EDX spectroscopy (Oxford X-Max^N System integrated in Zeiss GeminiSEM 500). Sample sizes of 2-3 g of the dried solid black liquor were investigated by XRF spectroscopy to get a quantitative analysis of the elemental composition. For SEM-EDX small amounts of sample (few milligrams) were analyzed under different resolutions. Then a mean value was calculated from the different results of the quantitative analysis. The pictures taken with the SEM were colored with different colors for each element. It is possible to get an insight into which salts are mainly present in the dried matter from these pictures.

Chemical Oxygen Demand (COD)

Chemical oxygen demand of the back liquor was obtained using NANOCOLOR™ COD Tube Tests from Macherey-Nagel™, using a potassium dichromate method. The black liquor was diluted with deionised water to the calibrated concentration range, and 1 mL added to the potassium dichromate solution. The samples were gently shaken and placed in a heating block (2 h, 148 °C). After heat treatment, the samples were removed from the heating block, re-homogenised and left to reach room temperature. The COD was determined on a UV/Vis spectrophotometer (NANOCOLOR™ UV/Vis II, 190-1100 nm). Analyses were performed in triplicate and standard deviation calculated.

Ash content

At PSI the ash content (wt.%) was determined by calcining in air the black liquor samples (ca. 20-25 g), in ceramic crucibles using the following procedure:

1. Heating ramp of 5 °C min^{-1}to 900 °C
2. Isothermal, 4h at 900 °C
3. Samples are cooled down to ca. 100°C, the crucibles are transfer to a desiccator until room temperature and are then weighted and compared with empty crucible weight.

For accurate measurements and standard deviation, the ash content was measured in triplicate for and the standard deviation calculated.

At KIT, the ash content of the dry matter black liquor was determined at 550 °C, 815 °C and 1000 °C with a Leco TGA-701.

1. Heating ramp of 5 °C min^{-1}to 105 °C under air; isothermal for 2 hours (drying)
2. Heating ramp of 5 °C min^{-1}to 250 °C under air; isothermal for 1 hour (removing of attached volatile organic compounds)
3. Heating ramp of 5 °C min^{-1}to 550 °C under air; isothermal for 2 hours (first determination of ash content)
4. Heating ramp of 10 °C min^{-1}to 815 °C under oxygen; isothermal for 1 hour (second determination of ash content)
5. Heating ramp of 10 °C min^{-1}to 1000 °C under oxygen; isothermal for 1 hour (third determination of ash content

High Heating Value (HHV)

HHV values of the dry matter of the black liquor were obtained using a bomb calorimeter (model C1, IKA) operating at 22 °C, with 30 bar of pressure of O_2 gas. The calorimeter was calibrated prior to measurements by combusting known quantities of benzoic acid.

HHV calculation from COD and from different equations (see references)

4 Results

Table 2. Pristine Black Liquor composition and properties. Values to be considered with caution are place between brackets [.] and commented in the additional notes.

Analysis	**Unit**	***Instrument used***	**Results from KIT**	**Results from PSI**
Dry matter content (DM)[1]	wt%	*Mass*	14.52	14.48
Density	kg.L^{-1}		1.0725±0.0001	
pH		*pH meter (25°C)*	13.31	
Viscosity	mPa*s	*Viscometer (20°C)*	2.4	
		Viscometer (50°C)	1.23	
Conductivity	mS.cm^{-1}	*Conductimeter (26°C)*	-	75.5
Chemical Oxygen Demand (COD)	g$_{O2}$.L^{-1}	*Spectrophotometry*	-	140.1±1.1
High Heating Value (HHV)[2]	kJ.L^{-1}	*Calculated*	-	1800±13
Total C	wt%	*CHNS*	4.4	4.7±0.3
	wt%	*TIC/TC*	[5.8±0.1]	4.9±1.5
TOC	wt%	*TIC/TC*	[5.5±0.3]	4.7±1.5
Total H	wt%	CHNS	12.1	
Total N	wt%	*CHNS*		0.08±0.01
Total S	wt%	*CHNS*	0.7	0.63±0.04
Sulfide	mg$_{S}$.L^{-1}	*Spectrophotometry*		
Chlorine	mg$_{Cl}$.L^{-1}	*Calculated (EDX)*	747	
		Calculated (XRF)	913	
Halides	mg$_{X}$.L^{-1}	Coulometric (TX)	942	
	mg$_{X}$.L^{-1}	Coulometric (AOX)	37	
Chloride	mg$_{Cl^-}$.L^{-1}	*Calculated (TX - AOX)*	905	

[1] Also refered to as solid content

[2] calculated from the COD (Vogel et al. 2000)

Table 3. Composition and properties of the Black Liquor dry matter. Values to be considered with caution are place between brackets [.] and commented in the additional notes.

Analysis	**Unit**	***Instrument used***	**Results from KIT**	**Results from PSI**
Total C	wt%	*CHNS*	34	[27.8±0.1]
Total N	wt%	*CHNS*	<0.1	[0.07±0.01]
Total S	wt%	*CHNS*	4.7	[3.4±0.4]
Total H	wt%	*CHNS*	3,4	[4.1±0.4]
Total Ash	wt%	*TGA*	72.9 (550 °C) 42.2 (815 °C) 36.1 (1000 °C)	34.0 (900 °C)
Total O[1]	wt%	*Calculated[3]* *EDX*	38.79 34.7±0.6	[30.56]
Total C	wt%	*EDX*	[42±3]	
Total Na	wt%	*EDX* *ICP*	17.0±2.3 17.73	
Total S	wt%	*EDX* *ICP*	4.4±0.4 4.65	
Total K	wt%	*XRF* *EDX* *ICP*	1.79 1.3±0.1 1.28	
Total Cl	wt%	*XRF* *EDX*	0.586 0.5±0.3	
Total Si	wt%	*XRF* *EDX*	0.243 0.4±0.2	
Total Rb	wt%	*XRF*	0.0360	
Total Ca	wt%	*XRF* *EDX*	0.0977 0.05±0.05	
Total Mg	wt%	*EDX*	0.02±0.02	
Total Al	wt%	*EDX*	0.02±0.02	
Total Fe	wt%	*XRF*	0.027	
Total Mn	wt%	*XRF*	0.014	

Total P	wt%	*XRF*	0.007	
High Heating Value	MJ.kg^{-1}	*Calorimetric bomb*		12.4±0.1
	MJ.kg^{-1}	*Calculated from* C_{org}, C_{in}, *H, O, N, S[2]*	10.21	
	MJ.kg^{-1}	*Calculated from [3]*	14.0	
	MJ.kg^{-1}	*Calculated from COD & DM*		18.4±1.3

[1] Calculated by difference PSI: O% = 100% -C% -N% -H% -S% -ash% ; KIT: O% = 100% -C% -N% -H% -S% - Na% - K% (CHNS from CHNS analysis, Na & K from ICP-AES).

[2] Calculated as described in (Wilson 1972).

[3] Calculated as described in Vakkilainen (1999).

4.1 Additional Notes

CHNS analysis pristine BL (KIT): Pristine black liquor CHNS analysis had an error with the nitrogen content, therefore it is missing.

TC/TIC (KIT): Results seem to be too high in comparison to all other carbon content analysis in the pristine BL. The analysis will be repeated later.

XRF, EDX, ICP dried BL (KIT): The XRF analysis shows low results for sodium and sulfur. Since the ICP and EDX results fit together very well, they are probably more reliable. EDX analysis has in some cases relatively high standard deviations. A possible explanation is the difficulty to get a good homogeneous sample. During the ICP analysis the measurement was repeated three times. However, the standard deviation is much smaller than the possible deviation due to daily calibration (up to 5 %).

CHNS and HHV dried BL (PSI): Might be underestimated as a result from moistening of the dry matter prior weighting. The analysis will be reproduced (or: have suffered from moistening) with a special care given to exposure to air moist prior analysis.

4.2 GPC Results

Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) separate the component mixture based on their size or more precisely on the hydrodynamic volume. It is a separation technique solemnly based on the diffusion velocity of the molecules through the column. There are no interactions (neither physical nor chemical) with the solid phase like in other chromatographic techniques. Larger molecules cannot enter the pores of the solid phase and hence pass the column fast. Small molecules however can diffuse in the pores and have a longer mean way through the column and get eluted later than the bigger molecules. Therefore, the hydrodynamic volume of a molecule change with the solvent. Molecules with side chains are also hard to investigate with GPC, because the chemical folding of the molecule can deliver a similar hydrostatic volume to other molecules with no side chains. The idea of GPC measurements is to compare the lignin size distribution of the original BL with the degradation products of the HTL of BL. For every peak in the calibration range the system calculates the number average molecular weight M_N and the weight average molecular weight M_W. The ratio of M_W to M_N is the polydiversity index (PDI) which gives an information about the distribution of the molecular weight in the sample (or in one peak of the sample). If PDI is equal to 1, it is monodisperse. In following the GPC of BL is presented and in the ongoing project the decomposition products from HTL are compared with this measurement:

First the sample preparation started with the acidification of pristine BL up to pH < 3. The solid content precipitating at this point was filtrated and centrifuged. Afterwards it was dried for 24 hours at 105 °C. Then 1.5 mg of the dried matter was diluted in 1.5 mL or 15 mL dimethyl sulfoxide (DMSO). For the analysis a diode array detector DAD L-2455 and two columns (Viscotek A4000 and A2500, one for bigger molecules one for smaller ones) were used.

Table 4. Results of the GPC analysis of the precipitated Black Liquor

Peak (Retention Volume in ml)	**8.873**	**9.513**	**10.922**	**12.248**	**15.399**
M_N (g/mol)	11236	2703	1341	1100	(0)
M_W (g/mol)	15206	3139	1341	1114	(86)
PDI (M_W/M_N)	1.353	1.161	1.000	1.012	(640098.125)

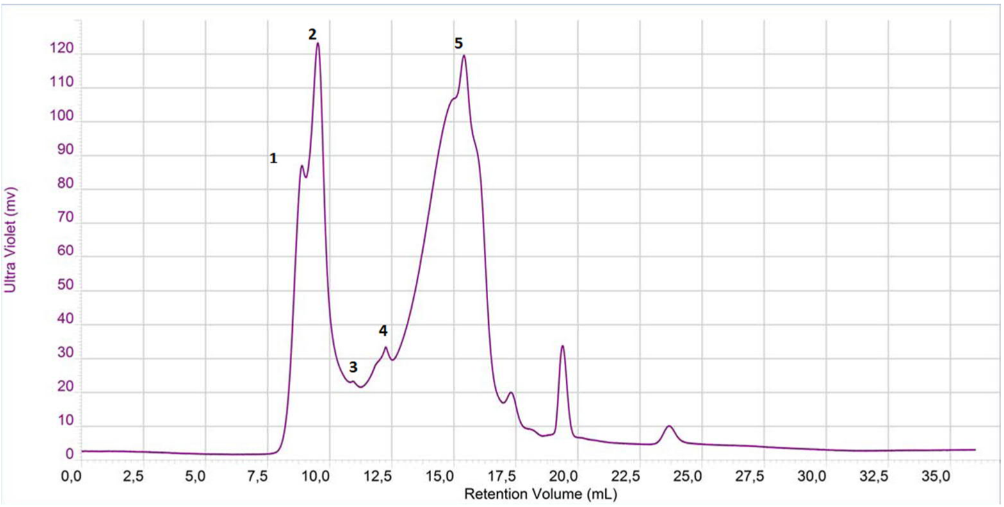

Figure 1. UV signal of investigated precipitated BL

The figure above shows the detection signal (here the UV) along the retention volume (mL). In the case of the investigated BL, there were five peaks found in the calibration range. Peak 5 lays too close to the calibration limit, therefore the values in Table 3 are not reliable. This graphic will be the base for all comparisons with the gained products later in this project. The intention is to observe shifting to smaller molecular weights. Later small molecules are observed by GC-FID/MS.

5 Discussion and Future research

Aging of black liquor is very relevant as this feedstock is sensitive to oxygen (e.g. sulfide oxidation) and temperature (e.g. hydrolysis and condensation reaction). For that reason, samples should always be stored in an air-tight PE or PP container at 1-5°C and the overhead meticulously purged with an inert gas.

Although it was not possible to quantify halogens individually (only Cl, Br, I together), chlorine represent the large majority as shown by the absence of halogen signal beside chloride in some analysis. The calculation of the Cl content based on XRF and EDX analysis of the dried matter gives results in the same range, indicating adapted and accurate analytical method. Furthermore, the calculated value from the organic halides (AOX) subtracted to the total halogen concentration represent the chloride content in a good approximation.

The ICP-AES analysis of the dried BL worked very well. The results are in the range of other studies of different BL. Also, the values from EDX analysis and IPC-AES are close together. Combined with the values from the CHNS analysis they show good reliable data for upcoming works.

Very different procedures were used at KIT and PSI for ash content analysis. The isothermal time is critical and very different from one test to the other. Also, TGA uses small amount of samples which causes an error in case the sample is heterogeneous. Although the results are close to each other, a standardization of the ash content measurement is required.

Drying 24h at 105°C ensures complete drying of the dry matter but will favor oxidation of sulfide and eventually other compounds. The extent of this oxidation is not known, but pure sulfide is known to oxidize fast in the presence of oxygen and water. A short drying (4h, no difference of weight detected) might limit that negative effect. In order to prevent moisture, increase of the dried matter in air, which would lead to an underestimation of C, N, S concentrations and HHV values, the storage of the dried BL in a desiccator is advised. To confirm the results obtained by KIT, PSI will shortly have CHNS of the dry matter (re)analyzed.

HHV measured at PSI on the dry matter using a calorimeter is reliable value for the dry matter analysis. However, the volatile compounds present in black liquor are not accounted for in such analysis as they are lost during the drying step. In addition, oxidation the sample is very likely to occur during the drying of black liquor. According to (Olsson et al. 2000) volatile organic compounds (VOC) constitute a significant part of the chemical oxygen demand (COD) loss from the kraft mill, a significant part is found in evaporation condensates. To circumvent that, COD can be used to estimate the HHV of the pristine BL hence accounting for all oxidizable matter, assuming that all organic matter can be efficiently chemically oxidized by the dichromate reagent. However, while very versatile, the compatibility of the method used has not yet been controlled with black liquor. This will be done by redissolving black liquor dry matter to measure its COD and compare the HHV calculated with the measured HHV of the dry matter.

CHNS and HHV analysis (Table 3) on the dry matter will be repeated at PSI following the same drying procedure that KIT used. Values slightly higher are expected to be obtained.

To better evaluate the contribution of VOC to the heating value of weak (pristine) black liquor, black liquor will be dried at 105°C in a setup equipped with a condenser to collect all VOC as described in (Olsson et al. 2000). The condensate collected should then be analysed (at least) for COD to determine the condensate's HHV, while the HHV of the dry matter should be analyzed with a calorimeter.

Storage of black liquor is problematic as described above. Some of the analysis should be repeated in the near future, maybe before starting with the liquefaction experiments, to evaluate how the black liquor evolved over time. This will be critical to control that change in a biocrude composition is related to a change in HTL process conditions and not related a potential change in feedstock composition.

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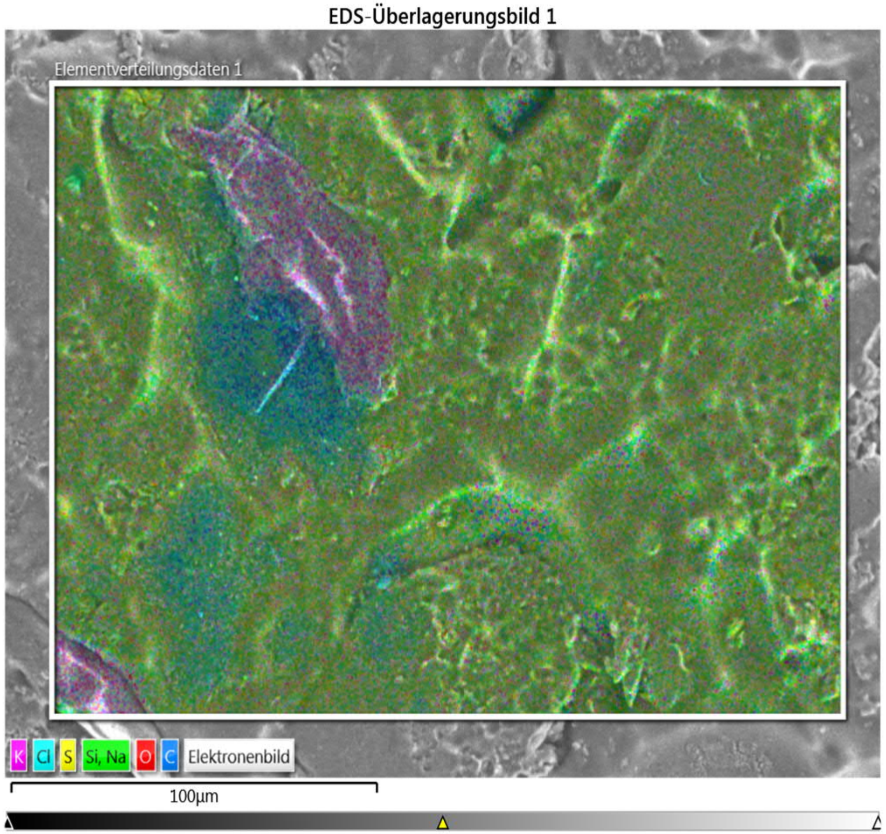
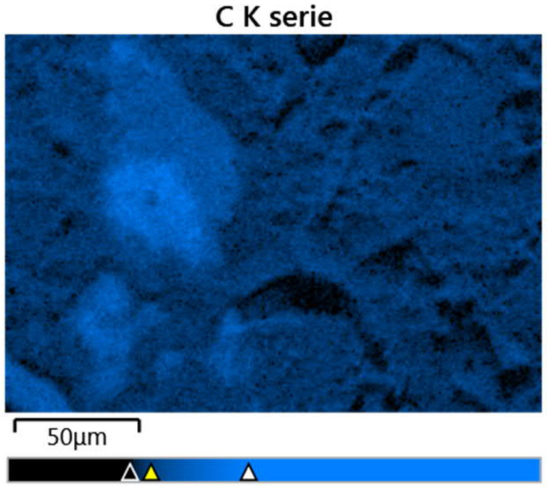
7 Appendixes

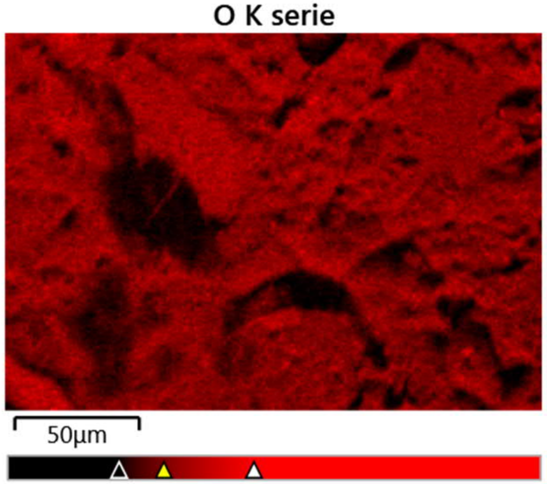
SEM-EDX determines elemental compositions as presented in the results as well as pictures from SEM with illustration of the positions of individual elements. In following link SEM images are shown, i.e. the overall image with all elements as well as images showing the position of NaCl, lignin and Na_2SO_X/Na_2S or NaOH.

KIT PowerPoint presentation of the SEM pictures with EDX analysis:

REM-EDX pictures


EDS-Überlagerungsbild 1

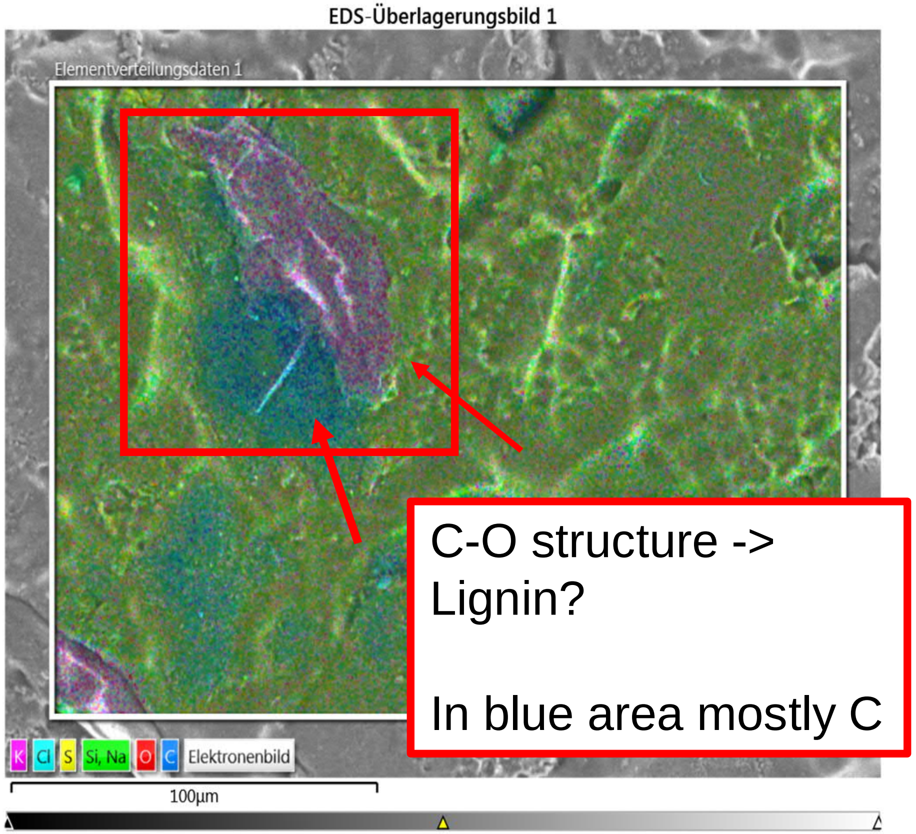

C K serie


O K serie

REM-picture with only one element

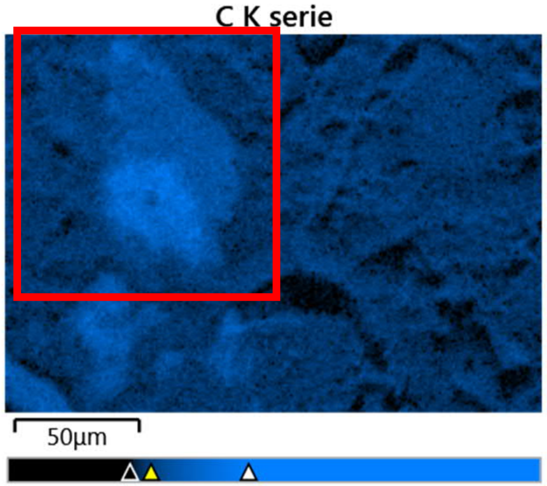
REM-Picture with all elements

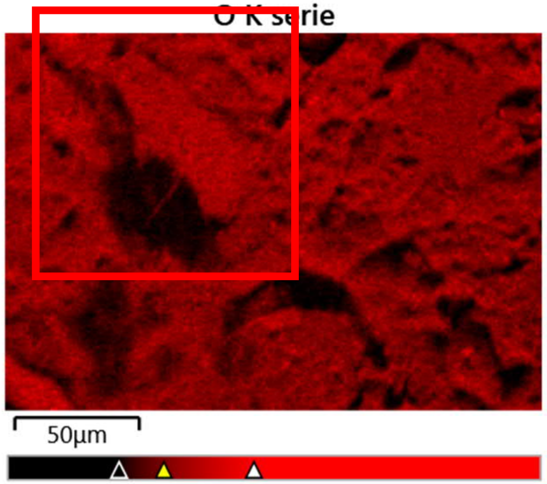
REM-EDX pictures



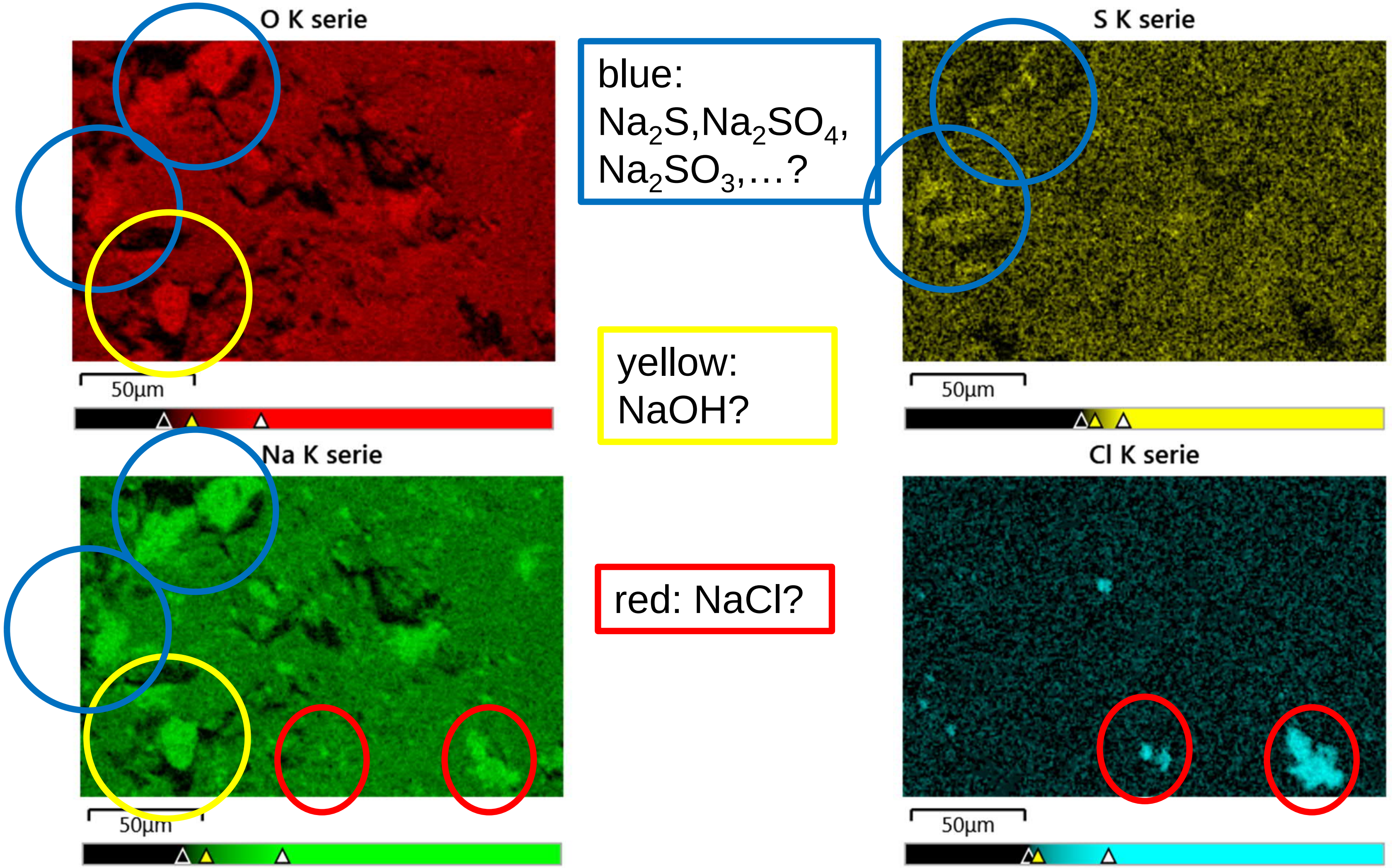
C-O structure -> Lignin?

In blue area mostly C





REM-EDX pictures



blue:
Na_2S,Na_2SO_4,
Na_2SO_3,…?

yellow:
NaOH?

red: NaCl?