Evaporation of lignin-lean black liquor

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ABSTRACT: Many of the pulp mill biorefinery concepts recently presented include removal of lignin from black liquor. In this work, the aim was to study how the change in liquor chemistry affected the evaporation of kraft black liquor when lignin was removed using the LignoBoost process. Lignin was removed from a softwood kraft black liquor and four different black liquors were studied: one reference black liquor (with no lignin extracted); two lignin-lean black liquors with a lignin removal rate of 5.5% and 21%, respectively; and one liquor with maximum lignin removal of 60%.

Evaporation tests were carried out at the research evaporator in Chalmers University of Technology. Studied parameters were liquor viscosity, boiling point rise, heat transfer coefficient, scaling propensity, changes in liquor chemical composition, and tube incrustation. It was found that the solubility limit for incrustation changed towards lower dry solids for the lignin-lean black liquors due to an increased salt content. The scaling obtained on the tubes was easily cleaned with thin liquor at 105°C. It was also shown that the liquor viscosity decreased exponentially with increased lignin outtake and hence, the heat transfer coefficient increased with increased lignin outtake. Long term tests, operated about 6 percentage dry solids units above the solubility limit for incrustation for all liquors, showed that the heat transfer coefficient increased from 650 W/m^{2}K for the reference liquor to 1500 W/m^{2}K for the liquor with highest lignin separation degree, 60%.

Application: This study can be used to help assess the consequences for an evaporation plant concerning both changes in capacity and risk for fouling when evaluating a biorefinery concept, including lignin removal, at a mill. It also adds novel information to the research work on black liquor evaporation.

Interest in the biorefinery concept for the pulp and paper industry has rapidly increased in recent years. The concept involves producing marketable products like pulp, paper, heat, power, fuels, and chemicals in a sustainable way, turning the traditional pulp and paper mill into a multi product biorefinery. A key challenge in this transformation is to extract the lignin from the black liquor in a way that it can be used in a more valuable application than is currently the case. Refined lignin can be used for producing high-end products such as low cost carbon fiber, phenols, or bioplastics, or it can be used as a fuel to replace oil in the lime kiln or coal/wood/bark in a power boiler, for example.

In recent years, the LignoBoost process has been developed as a technique to separate lignin from black liquor [1,2]. In this process, lignin is extracted from black liquor by precipitation, filtration, and washing. When removing a part of the lignin, the chemistry of the black liquor naturally changes. Both the organic and inorganic chemistry will change, and that will influence many of the important process parameters in the black liquor evaporation plant. By removing the organic lignin, the viscosity of the black liquor will change. Viscosity is the single most important parameter determining the heat transfer in black liquor evaporators, and thus, the heat transferred will be largely affected by removing lignin from the black liquor. By changing the inorganic chemistry, the scaling propensity is affected, as well as the dry solids content at which crystallization will start.

The aim of this study was to investigate how the change in liquor chemistry affected the evaporation of black liquor when lignin was removed. The highlighted parameters of interest were liquor viscosity, boiling point rise (BPR), heat transfer coefficient, scaling propensity, changes in liquor chemical composition, and tube incrustation.

EXPERIMENTAL

Experimental procedure

Softwood kraft black liquor from a Swedish pulp mill was sent to LignoBoost Demo AB in Bäckhammar, Sweden, for lignin removal. Different fractions of filtrate from the lignin removal process and black liquor were then mixed to mimic a full scale case at a pre-determined lignin removal rate. In the evaporation trials, four different black liquors were studied: one reference black liquor (with no lignin extracted); two lignin-lean black liquors with a lignin removal rate of 5.5% and 21%, respectively; and one liquor with maximum lignin removal of 60%.

The evaporation experiments were conducted in the research evaporator at Chalmers University of Technology, Gothenburg, Sweden, as described in the following sections. Chemical analysis of liquor samples and scaling material were analyzed at MoRe Reserch, Örnsköldsvik, Sweden. The gross calorific value was determined at SP, Borås, Sweden.

Research pilot evaporator

The main component of the evaporator is a vertical tube, 60 mm in diameter and 4.5 m long, with the falling liquor film on the outside. The liquor is heated with steam condensing on the inside of the tube. The heating steam is distributed along the inside of the evaporator tube through an internal steam tube. The steam condensing on the inside of the evaporator tube forms a falling film. The liquor is fed to the top of the evaporator using a circulation pump (**Fig. 1**).

The liquor on the tube flows downwards while being evaporated, and the produced vapor is separated from the liquor in the flash tank. The bottom of the flash tank is connected to a circulation pump. The liquor vapor is fed to the condenser, which regulates the pressure. The produced condensate can be ejected to an external container, placed on a scale, or re-circulated to the flash tank to keep the dry solids content constant.

The measured data of interest from the pilot evaporator are:

- Liquor circulation rate
- Refractive index of the circulating liquor
- Density of the circulating liquor
- Viscosity of the circulating liquor
- Pressure and temperature of both the steam and the liquor side
- Heating steam condensate volumetric flow

All measurements devices are sampled every minute. In the evaporator, a number of parameters are controlled. The steam pressure and the liquor pressure are regulated by two control valves, and the circulation flow is controlled by the number of revolutions of the circulation pump. Sight glasses are mounted at four positions: one each at three different heights on the evaporator tube, and one on the flash tank. In the sight glasses, there is a possibility to visually observe the liquor falling film and the formed scales.

The experimentally determined liquor heat transfer coefficient is based on the steam condensate mass flow rate and the measurement of the temperature difference between the steam and liquor. The heat transfer coefficient is then used to calculate the overall heat transfer coefficient, U, from Eq. (1):

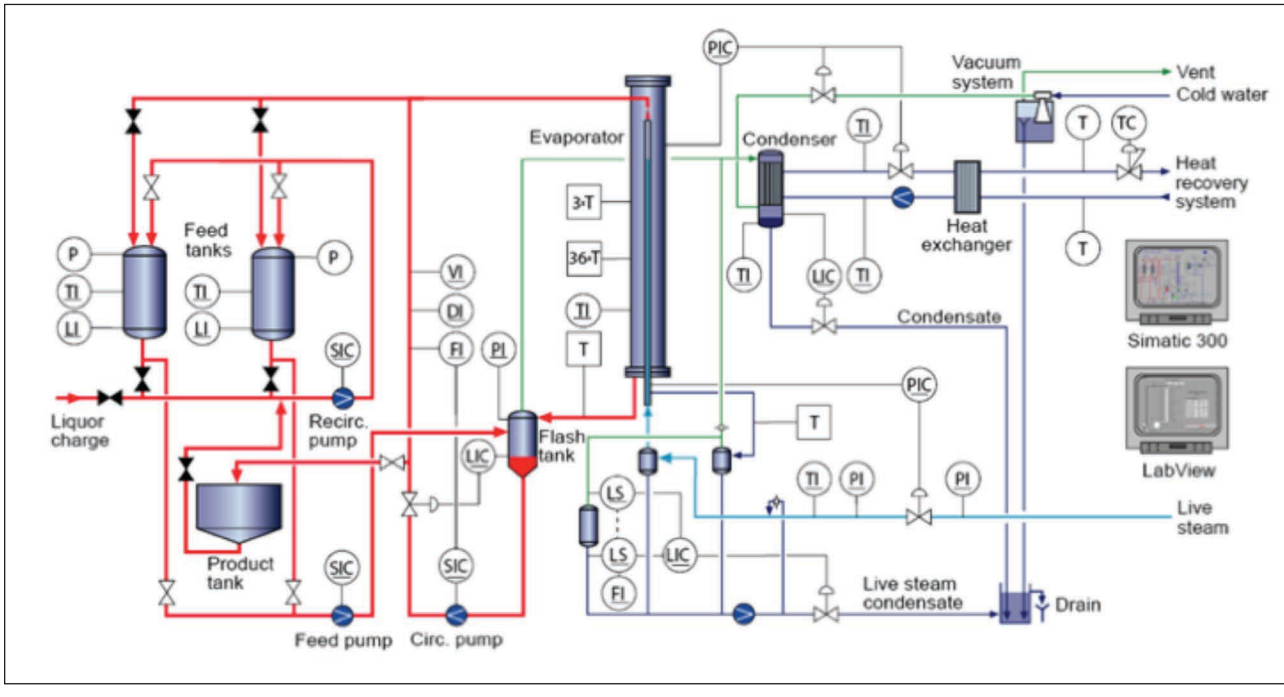
$$\frac{1}{UA_o} = \frac{1}{h_i A_i} + \frac{\delta_w}{k_w A_m} + \frac{1}{h_o A_o} \quad (1)$$

where h_i was calculated using a correlation for condensation on vertical surfaces by Schnabel and Palen [3], k_w is the steel conductivity and δ_w is the tube thickness (1 mm).

Evaporation tests

The evaporation study was divided into two tests:

1. *Determination of the black liquor meta solubility level, i.e., at which level of dry solids the scaling material starts to precipitate.* The evaporator flash tank was 100% filled with ~30% dry solids, and during the evaporation process, the liquor condensate was continuously measured externally, meaning there was no feeding of liquor to the effect and no product liquor flow from the effect. The meta solubility level was determined through several process parameters such as density, refractive index, and liquor phase particles.



1. Schematic flow sheet of the research evaporator at Chalmers University of Technology.

		Standard	Standard Name	Reference	5.5%	21%	60%
pH		SS 028122	Water quality - Determination of pH	13.5	13.5	12.8	9.9
Dry solids	%	SCAN-N 22	Black liquor - Dry matter content and fiber content	31.4	29.0	27.1	23.2
Na	g/kg ds	SCAN-N 37	Black liquor - Sodium and potassium contents	215	217	223	261
CO_3	g/kg ds	SCAN-N 32	White, green and black liquors and burnt lime sludge - Carbonate content	66	76	93	157
SO_4	g/kg ds	SCAN-N 36	Black liquors and sulfite spent liquor – Sulfite, sulfate and thiosulfate ion concentrations	18	26	38	92
S_2	gS/kg ds	SCAN-N 31:94	White, green and black liquor – Hydrogen sulfide ion concentration	9.5	3.4	4.8	2.2
S_2O_3	g/kg ds	SCAN-N 36	Black liquors and sulfite spent liquor – Sulfite, sulfate and thiosulfate ion concentrations	8.8	43	40	38
S_{tot}	g/kg ds	SCAN-CM 57	Pulp – Total sulfur content	34	28	33	42
K	g/kg ds	SCAN-N 37	Black liquor – Sodium and potassium contents	15.8	16.3	16.9	19
C_2O_4	g/kg ds	SCAN-N 39:05	Process liquors from bleached plants - Dissolved and precipitated oxalate - Using ion chromatography	3.8	4.3	4.4	4.9
Ca_{tot}	g/kg ds	SCAN-N 38	Black liquor – Acid-soluble metals	0.23	0.20	0.20	0.08
$Ca_{soluble}$	g/kg ds	KA11:004	Chemical Analyze 11:004 (MoRe Research AB)	0.19	0.12	0.11	0.05
RA	gNaOH/kg ds	SCAN-N 33:94	Black liquor – Residual alkali (Hydroxide ion content)	45	46	14	<0.9
COD	g/kg ds	SS 028142	Determination of chemical oxygen demand in water - COD^{Cr} oxidation with dichromate	960	871	785	512
Lignin	g/kg ds	KA 11.202	Chemical Analyze 11:202 (MoRe Research AB)	491	466	387	170
***Na_2CO_3**	g/kg ds			116	134	165	277
***Na_2SO_4**	g/kg ds			26	38	57	136
***Na_2CO_3+Na_2SO_4**	g/kg ds			142	172	222	413
***Na_2CO_3+Na_2SO_4**	g/kg H_2O			65	70	82	125
CO_3/ (CO_3+SO_4)	mol/mol			0.85	0.83	0.80	0.73
HHV	MJ/kg ds	Calorimeter		13.2	13.0	11.3	7.4
LHV	MJ/kg ds			12.5	12.2	10.6	6.9

The inorganic-to-organic (lignin) mass ratio starts at 0.7 for reference liquor, 0.8 for with 5.5% removal, 1.1 for 21% removal, and 3.3 for the liquor with 60% removal. Although not shown in Table I, the polysaccharide content in the prepared solutions was similar in relative composition. The major difference was the decreasing polysaccharide content (of total dry solids) going from reference solution 1.8% to 1.1% with the maximum lignin removal. The polysaccharide content, of total dry solids, in the reference liquor agrees with earlier reported literature values [5,6].

I. Initial chemical composition of the liquors.

2. *Evaporation scaling test with continuous black liquor feed of ~30% dry solids to the effect.* The produced black liquor dry solids level was chosen to be +6% dry solid units above the meta solubility level during the whole test, for the specific black liquor. The evaporated liquor condensate was returned to the flash tank to keep the dry solids level constant at the chosen level. The continuously scaling tests were run for ~24 h, which was sufficient enough time to create a 1-3 mm thick incrustation layer at the heating tube surface.

In the second type of tests, the heat transfer coefficient was adjusted for the change in physical properties with time. Both the change in viscosity and mass flow rate are accounted for by using Eq. (2):

$$h_{liquor}(t) = h_{liquor}(t) \cdot \frac{\Gamma(t=0)^{P_a}}{\Gamma(t)^{P_a}} \cdot \frac{\mu(t=0)^{P_b}}{\mu(t)^{P_b}} \quad (2)$$

where Γ is the mass flow rate and μ is the viscosity. The pa-

rameters P_a and P_b were set to 0.26 and -0.41 in accordance with Johansson et al. [4]. This is done to isolate the effect of fouling from the other factors, which also affects the heat transfer.

The evaporation parameters used during both tests were:

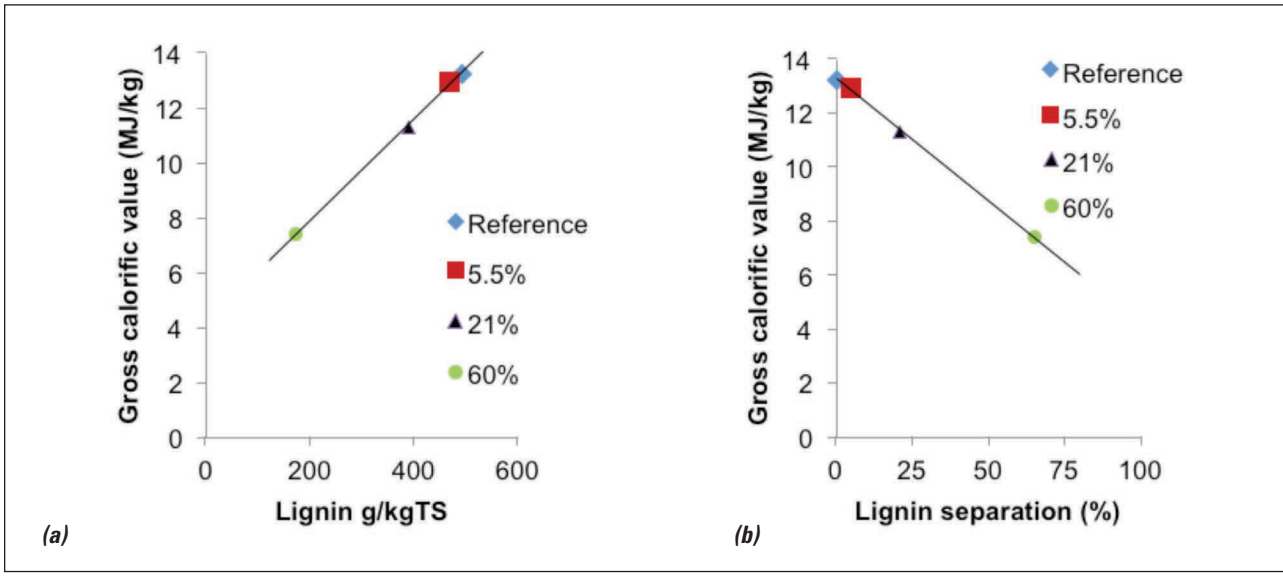
- Feed liquor temperature 65°C (test 2 only)
- Product liquor temperature 120°C
- Steam temperature 130°C
- Circulation flow ~1.3 kg/m*s (700 l/h)

During the tests, the following samples were taken:

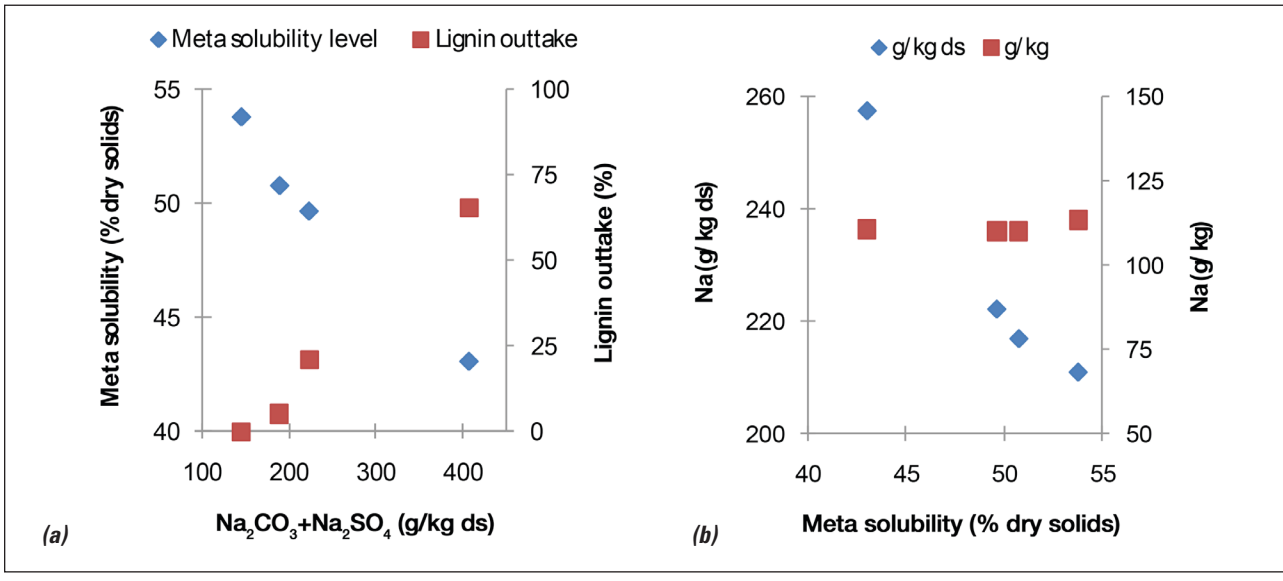
- Black liquor samples before test start and at several dry solid positions during both tests
- Liquor phase precipitated salt particles with inline sampling valve
- Incrustation material, after scaling tests, collected through the evaporator lower sight glass
- Liquor condensate during the continuously scaling test

Chemical properties of the liquors

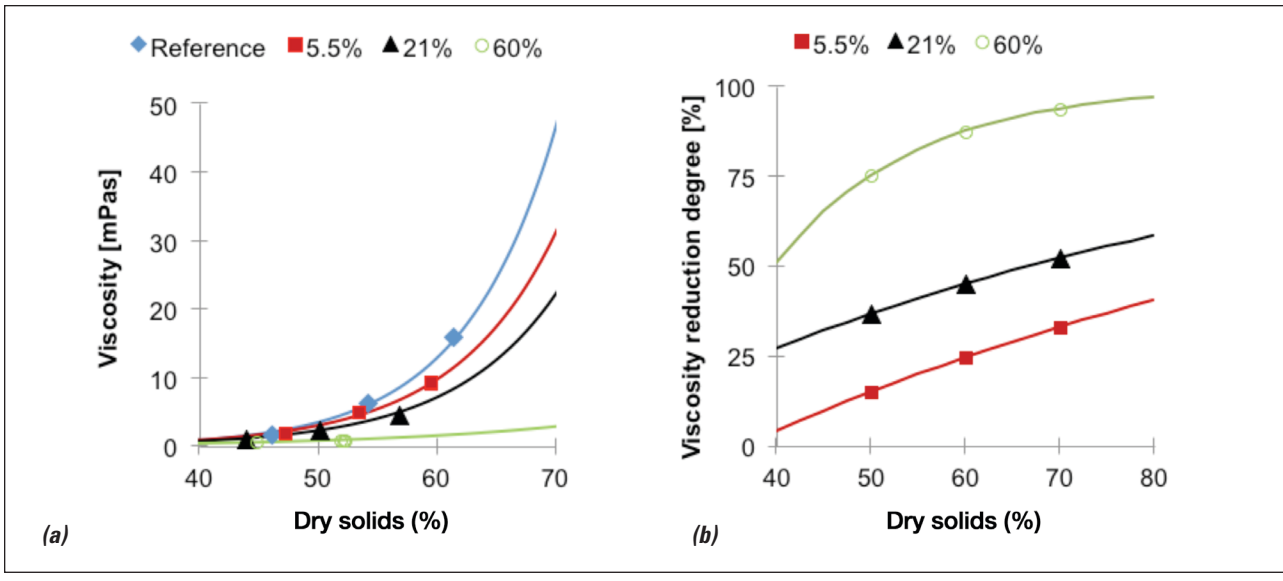
Table I describes the chemical composition of the liquors that were analyzed. It can be seen that the actual black liquor composition has changed while removing lignin. The major changes in the mixed solutions, compared to the reference liquor, are increased content of sulfates and thiosulfates, increased content of carbonates, and decreased content of lignin. The molar ratio of carbonate to sulfate in the reference



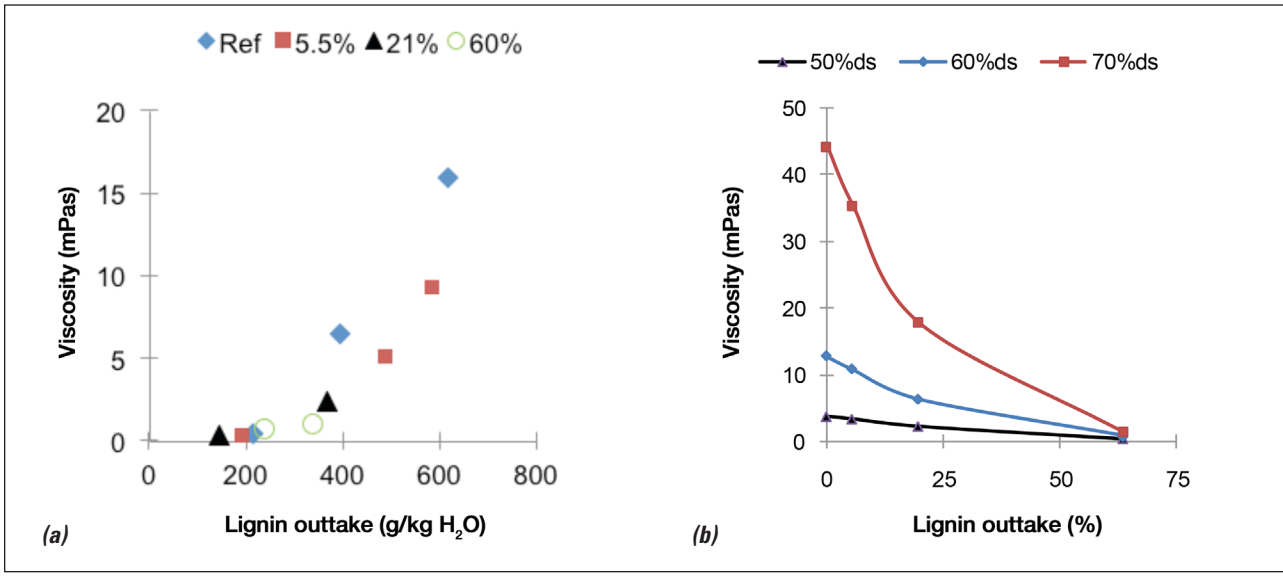
2. Reference and prepared black liquor gross calorific value dependence on a) lignin content and b) lignin separation degree.



3. a) Total solute Na_2CO_3 and Na_2SO_4 content at the apparent meta solubility level and total lignin outtake and b) solute sodium content at the meta solubility level.



4. Black liquor lignin separation effects on the liquor viscosity. a) Dots are measured values and full lines are curve fitted to the measured dots. b) Viscosity reduction degree of the tested liquors relative to the reference black liquor.



5. a) Liquor lignin content versus viscosity, and b) liquor viscosity effect due to lignin separation degree.

liquor was 0.85, but decreases with the degree of lignin removal down to a molar ratio of 0.77 for the liquor with maximum lignin removal (60%). This corresponds to the Na_2CO_3 to Na_2SO_4 ratio starting at a high level, 4, in the reference liquor but decreasing to 2 in the liquor with 60% lignin removal. The total Na_2SO_4 and Na_2CO_3 content in the reference liquor was 142 g/kg dry solids and increases up to 413 g/kg dry solids in the liquor with 60% removal.

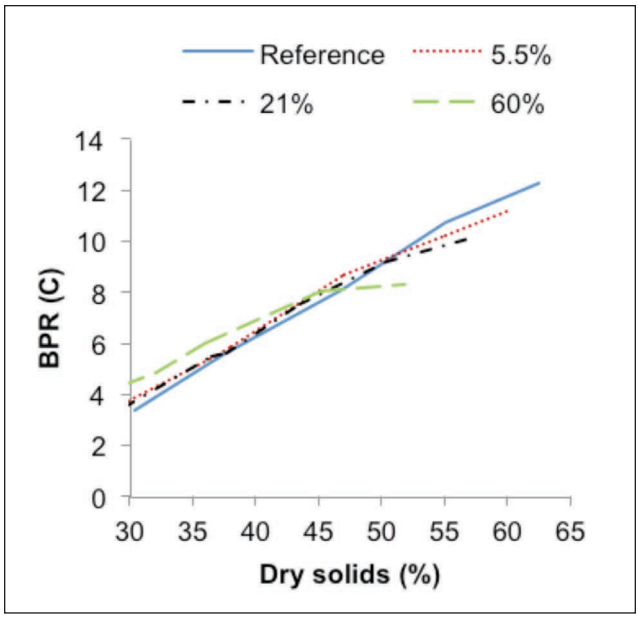
The inorganic to organic (lignin) mass ratio starts at 0.7 for reference liquor, 0.8 for 5.5% removal, 1.1 for 21% removal, and 3.3 for the liquor with 60% removal. Even though not shown in Table I, the polysaccharide content in the prepared solutions was similar in relative composition. The major difference was the decreasing polysaccharide content (of total dry solids) going from Reference solution 1.8% to 1.1% with the maximum lignin removal. The polysaccharide content, of total dry solids, in the reference liquor agrees with earlier reported literature values [5,6].

The Reference and the mixed black liquors gross calorific value shows a direct relationship with the actual liquor lignin concentration (**Figs. 2a** and **2b**).

EVAPORATION RESULTS AND DISCUSSION

Liquor meta solubility

The liquor meta solubility, dry solids level, where crystal particles start to precipitate in the liquor phase is important to know to meet the washing demands due to increased scaling propensity. The effect on the meta solubility is



6. The liquor dry solids effect on the boiling point rise (BPR) at 120°C. The change of the lines indicates the meta solubility level.

shown in **Fig. 3a**. Increased lignin outtake increases the total concentration of scaling elements in the liquor phase, which pushes the meta solubility level towards lower liquor dry solids.

As seen in Fig. 3b, there is a maximum of the solute sodium content before crystal particles start to precipitate around 110 g/kg solution. The meta solubility agrees quite well from this study with salt solution data performed at similar conditions [7]. The meta solubility is not only dependent on the total salt concentration, but also on the composition of the different elements, e.g., molar ratio.

Liquor viscosity

One important effect of lignin separation from black liquor is the change of the liquor viscosity [8]. In **Fig. 4a**, the inline, actual measured viscosity is presented as dots. The lines in the figure are described by the exponential expression:

Liquor viscosity (mPas)= K exp^A	(at 120 °C)
K= (0.00027 * lignin outtake%)+ 0.0075	
A= [(-0.0011 * lignin outtake%)+ 0.124] *	%dry solids

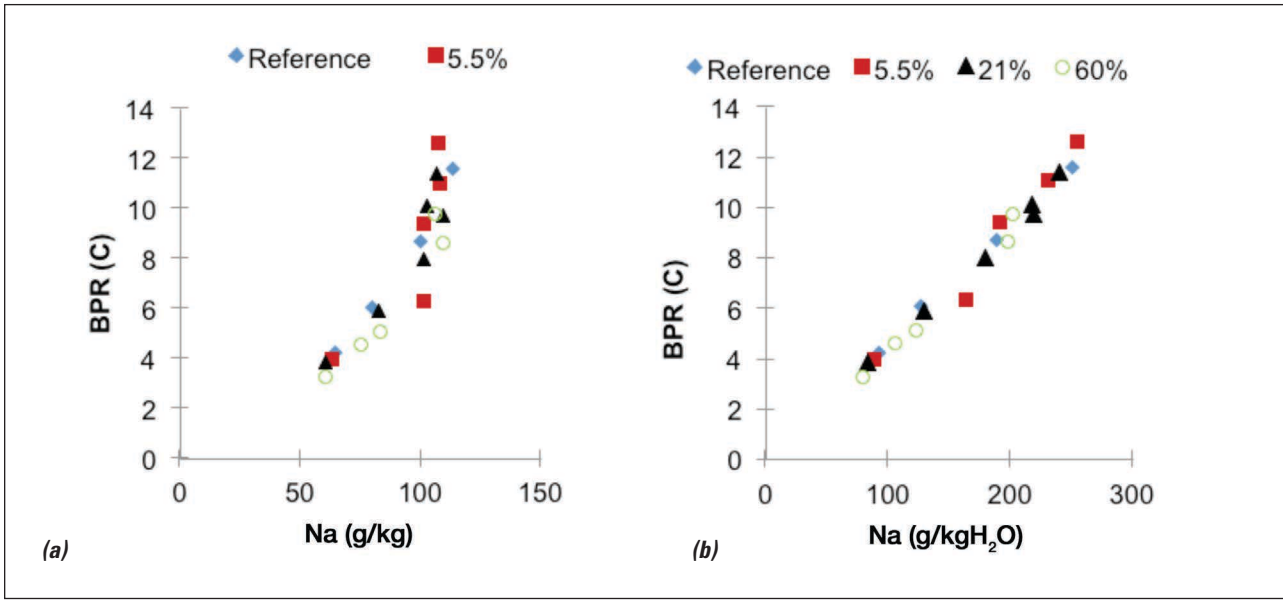
In **Fig. 4b**, the results are presented as the viscosity reduction compared to the reference liquor viscosity.

The actual liquor lignin content per kilogram of water shows that the liquor viscosity is mainly determined by the lignin content (**Fig. 5a**). An increased lignin separation degree markedly decreases the liquor viscosity, especially at higher dry solids (Fig. 5b).

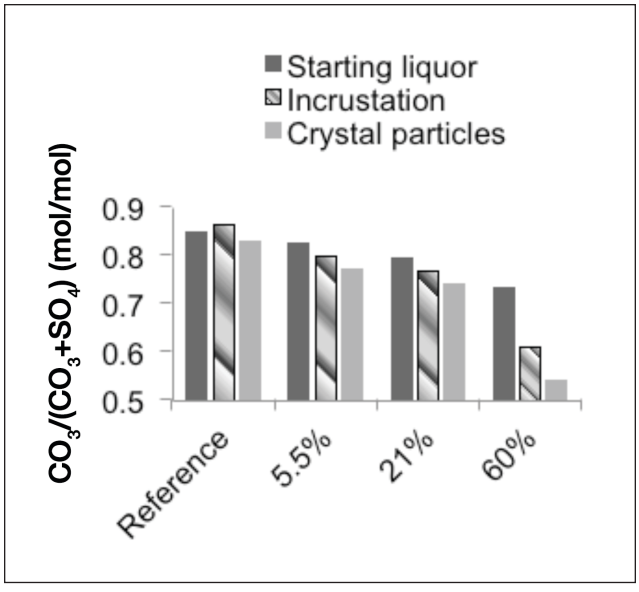
Boiling point rise

From all test runs, there are two distinct and separate BPR areas (**Fig. 6**). The disruption in the curve indicates the meta solubility level, i.e., the point where crystal particles start to precipitate (loss of sodium and sodium counter-ions from the system).

The parallel shift in BPR curves below meta solubility in 6 is caused by two reasons: 1) the increased salt concentration with increased lignin outtake; and 2) less organic material that bonds sodium elements, i.e., more sodium elements as solute ions, which decreases the water activity. The largest effect on the BPR comes from alkali earth metals like sodium and potassium, i.e., small ions with high charge density that have a large effect on water activity. In **Fig. 7**, the BPR is plotted against solute sodium content; i.e., precipitated sodium particles (above meta solubility level) are excluded.



7. a) The solute sodium content effect on the BPR, per amount of solution, and b) solute sodium content, per amount of water.



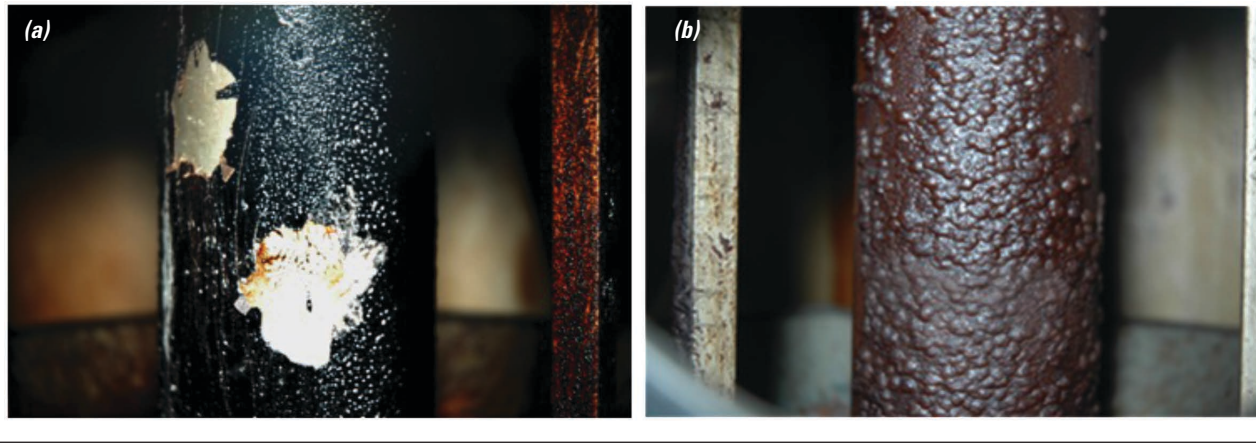
8. The sodium carbonate-to-sodium sulfate molar ratio of the starting liquors, scaling material, and precipitated liquor phase crystals (crystals during long term test).

Precipitated sodium particles have no effect on the water activity; i.e., crystals behave as inert material. In Fig. 7a, the sodium content per kilogram solution shows an upper level of sodium content. This level, around 110 g/kg solution, corresponds to the liquor meta solubility level. The BPR plotted against the sodium content per kilogram of water is found in Fig. 7b, which shows a direct connection between the BPR and the solute sodium content. This means that the solute sodium content can be used to describe the BPR at any dry solids content. The reported values agree well with earlier reported literature values [9].

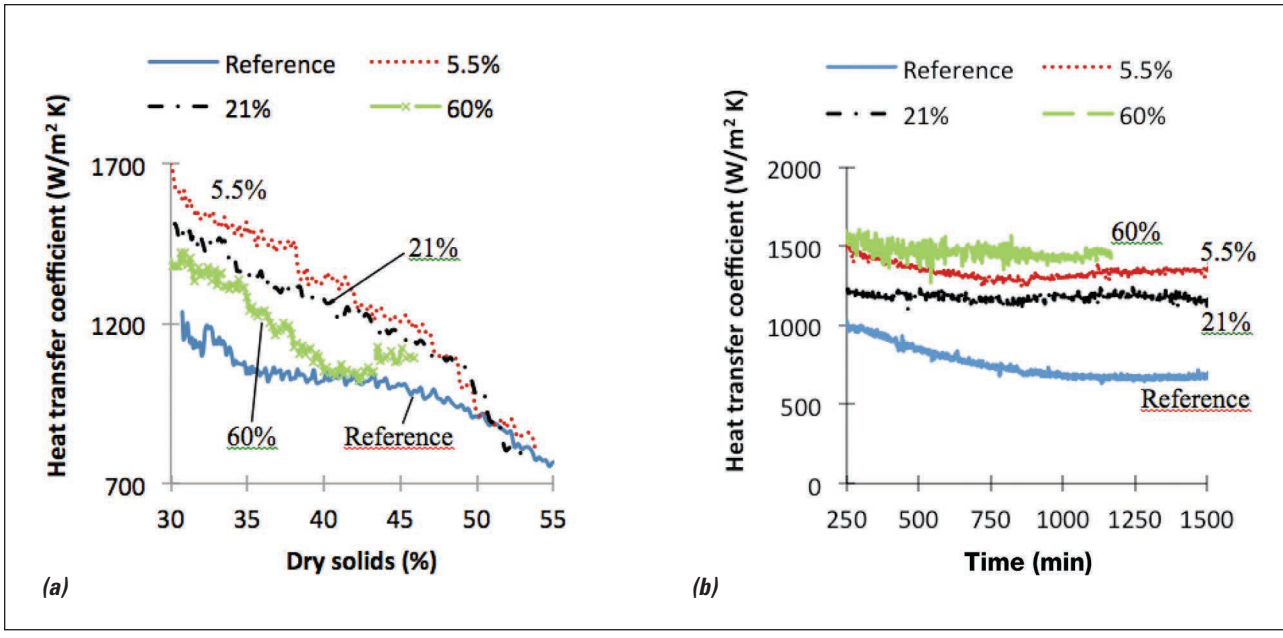
Scaling

The different tested liquors show, due to the lignin removal, changes in the liquor chemical composition in both inorganic and organic content. In Table I, it can be seen that the concentration in the liquors of the main scaling materials, such as sodium carbonate and sodium sulfate, increases with increased lignin outtake. In **Fig. 8**, the molar ratio is given for the liquors at test start, and then for particles in liquor phase and incrustation material at tube surface after the test. As seen in the figure, the carbonate-to-sulfate ratio is decreasing with lignin removal. The reference liquor shows a high content of sodium carbonate with possible particles and scaling composition of $6Na_2CO_3 \cdot Na_2SO_4$ [8,10].

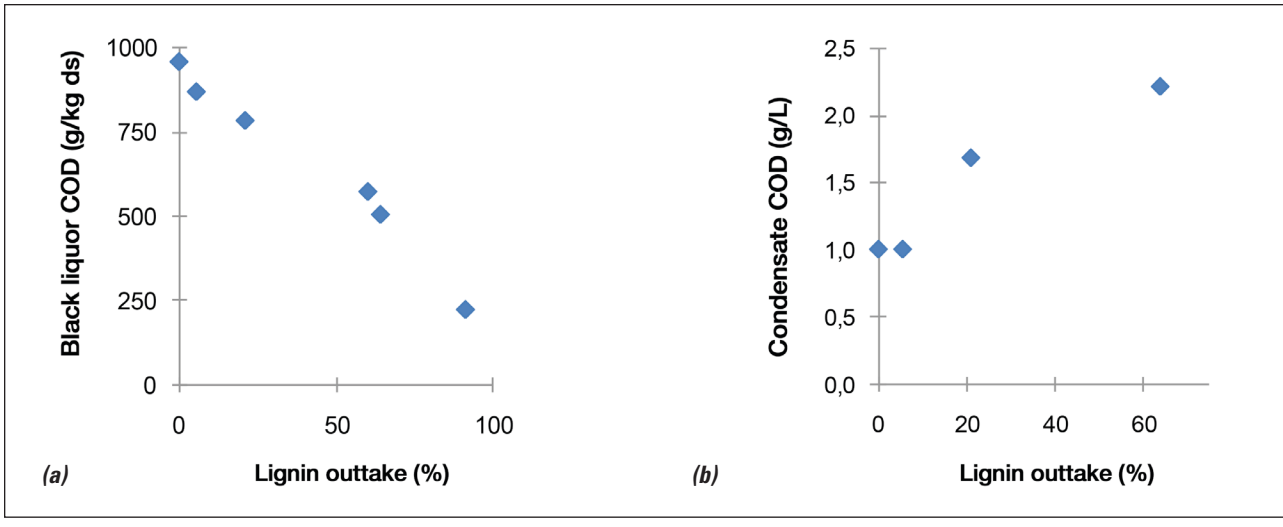
The initial molar ratio in the liquor sets the crystal composition being formed. In this case, the crystals will have a lower content of sodium carbonates compared to the original liquor due to the higher tendency of sodium sulfate to precipitate (after the first meta solubility level), which is seen in Fig. 8 as the carbonate-to-sulfate ratio decreasing in the "incrustation" and "crystal particles" compared to the "starting liquor." This behavior is accentuated during the test with the liquor with maximum lignin removal, where the scaling layer consists of an almost equal amount of sodium carbonate and sodium sulfate, whereas the initial liquor has more than 70% carbonate. One positive effect of the increased amount of sodium sulfate is the tendency toward forming larger precipitated crystal particles with higher degree of crystal mass in the liquor phase. Larger particles have lower tendency to precipitate on the tube surface and can also work as a growth nucleolus element for smaller particles, i.e., larger crystal mass fraction in liquor phase and not on the tube surface [11]. The thickness of the scaling layer on the tube surface was fairly similar for the different test runs, 0.2-3 mm, which is probably due to the short test time, 24 h. As seen in **Figs. 9a** and **9b**, the scaling formed with the lignin depleted liquors is less dark in color. During these tests, the tube surface was washed with thin liquor but no distinction in the washing behavior could be seen between the different types of formed scaling material. The sum of the amounts of sodium, carbonate, and sulfate in the incrustations was 852 g/kg in the reference



9. Scaling layer, at the tube surface, after long term test. a) Reference liquor, uncovered tube surface (lighter areas) is removed scaling material used for chemical analysis, 0, 5-1 mm. b) 60% lignin outtake, 0.2-3 mm.



10. a) Heat transfer coefficient up to the meta solubility level during test 1. b) Viscosity and mass flow corrected heat transfer coefficient during the second test. The final dry solids during test 2 were 62.5% for the reference liquor, 60.4% for the 5.5%, 56.9% for the 21%, and 52.2% for the 60% case.



11. a) Black liquor chemical oxygen demand (COD) content and b) condensate COD content versus actual lignin outtake.

liquor and 971 g/kg in the liquor with 60% lignin outtake. Thus, there are very little other substances present in the incrustation (3%-15%), even though the black and brown colors imply some other black liquor residues.

Heat transfer

The changes of the heat transfer coefficient due to the lignin separation are shown in **Fig. 10**. In Fig. 10a, the measured heat transfer coefficient is shown (as measured) up to the meta solubility level. It shows, as expected, a lower initial value of the reference liquor compared to the mixed liquors. As a consequence of the lignin removal and reducing the viscosity of the liquid (at the same solids content), it is expected that the heat transfer would increase with increasing lignin removal. Thus, the difference between the reference liquor and the liquor with maximum lignin removal was expected to be greater than indicated, due to the large viscosity difference, and the order of the three lignin-lean liquors was expected to be different. For all the liquors, the viscosity increases exponentially as the dry solids increase. Fig. 10b shows the scaling effects, compensated for increased viscosity and mass circulation flow, according to Eq. (2), from the individual long run tests.

For the reference liquor, the heat transfer coefficient starts at ~1200 W/m²K (clean tube) and falls to 1000 W/m²K when the meta solubility level is passed due to tube scaling. The 1200 W/m²K is a low value in the pilot, which could indicate

that the tube was not fully cleaned before starting. During the long run scaling test of the reference liquor, the dry solids level of the feeding liquor was 31.4% and the product liquor reached a dry solids level of 62.5%. The corrected heat transfer coefficient was stabilized at 650 W/m²K after a 17 h experiment (Fig. 10b). The scaling layer obtained showed a clearly reduced heat transfer value, which could be an effect of the higher carbonate content in the scaling layer (see incrustation bar for reference case in Fig. 8).

For the liquor with 5.5% lignin removal, the heat transfer coefficient starts at ~1700 W/m²K (clean tube) and falls to 1500 W/m²K when the meta solubility level is passed due to tube scaling. During the long run scaling test, the initial liquor dry solids level was 29.0% and the product liquor reached 60.4% dry solids. The corrected heat transfer coefficient was stabilized at 1350 W/m²K after 12 h.

For the liquor with 21% lignin removal, the heat transfer coefficient starts at ~1500 W/m²K (clean tube) and falls to 1400 W/m²K after the meta solubility level due to scaling. During the long run scaling test for that liquor, the dry solids level of the feeding liquor was 26.9% and the product liquor reached a dry solids level of 56.9%. The corrected heat transfer coefficient was stabilized at 1250 W/m²K after approximately 5 h. For this liquor, a second nucleation point appeared at 59.5% dry solids. For the other liquors studied, a second nucleation point was not detected, but could occur at higher solids content. This will affect the liquor viscosity, BPR, and heat transfer values.

For the liquor with 60% lignin removal, the heat transfer coefficient starts at ~1400 W/m²K (clean tube) and seems to increase after the meta solubility level is passed; however, the reason for this is not clear (probably due to the correction model used). During the long run scaling test, the initial liquor dry solids level was 23.5%, and the product liquor reached a dry solids level of 52.2%. The corrected heat transfer coefficient was stabilized at 1600 W/m²K after 7 h.

CHEMICAL OXYGEN DEMAND

The chemical oxygen demand (COD) content in the prepared black liquors shows a direct connection to the lignin content in the liquors. In **Fig. 11a**, the lignin outtake is plotted against the COD content in the liquor. The COD content in the condensate, taken during the long term tests, shows, however, increasing values with increased lignin outtake (Fig. 11b). The reason for this is unclear.

CONCLUSIONS

Three lignin-lean black liquors with 5.5%, 21%, and 60% lignin removal degree have been investigated and their evaporation characteristics have been compared to a reference black liquor with the following main findings:

- With increased lignin outtake, the sodium sulfate and sodium carbonate content in the black liquor increases per kg dry solids, whereas the molar ratio decreases from 0.85 in the reference liquor to 0.73 with the maximum lignin removal.

ABOUT THE AUTHORS

Many biorefinery concepts are being discussed at the moment in which lignin is being extracted from black liquor, which led us to investigate the evaporation properties of lignin-lean black liquors. We have a long tradition of research work with evaporators using normal black liquors. Until now, however, no study had been performed on lignin-lean black liquors.

The most challenging part of this study was its scale and its broad content, which involved everything from processing liquors to performing pilot-scale evaporation experiments and chemical analysis. Our most interesting finding was the positive effects of the lignin removal on the capacity of evaporators, as a consequence of the strong reduction in viscosity.

This information will help in the assessment of biorefinery concepts with lignin removal, as the consequences for the evaporation plant can be evaluated concerning both changes in capacity and risk for fouling.

Wallmo

Andersson

Wimby

Gourdon

Lignin extraction is only one of many biorefinery concepts, and we are interested in investigating other biorefinery residual streams in the future.

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- The gross calorific value decreased linearly with the lignin separation degree.
- The meta solubility level changes towards lower dry solids with increased lignin removal due to the increased salt concentration per kg of dry solids. The meta solubility level could also be described through the total sodium carbonate and sodium sulfate content.
- The liquor viscosity changes could be described through an exponential behavior of actual lignin outtake. At 50% dry solids, the liquor with maximum lignin outtake (i.e., 60% removed) showed a viscosity reduction of 75% compared to reference black liquor. The liquor viscosity was also shown to follow the lignin content per kilogram of water.
- Comparing the liquors at equal dry solids contents and below the solubility limit, increased lignin outtake somewhat increases the BPR as a consequence of the increased inorganic material. Above the meta solubility limit, the inorganic salts precipitate and the contribution to the boiling point rise declines.
- The heat transfer coefficient increased with increased lignin outtake, from 650 W/m²K with the reference liquor to 1500 W/m²K for the liquor with maximum lignin removal during long term tests, operated at dry solids content 6% above the corresponding solubility for each liquor.
- The tube scaling material and precipitated liquor phase crystal particles showed a similar composition of sodium carbonate and sodium sulfate composition as the starting liquor, except for the liquor with 60% removal where the crystals had lower carbonate content. The main scaling material was sodium carbonate and sodium sulfate.
- The tube was easily cleaned after full test time with thin liquor at 105°C, and no distinction between the formed scaling materials could be made. **TJ**

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