

EUCALYPTUS BLACK LIQUOR – DENSITY, VISCOSITY, SOLIDS AND SODIUM SULFATE CONTENTS REVISITED

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ABSTRACT

One of the greatest challenges in the recovery unit of the pulp and paper mills is to avoid sodium salt scaling in evaporators during black liquor concentration process. This scale formation on the heat transfer surfaces of evaporators and concentrators, due to precipitation of sodium salts, reduces the overall efficiency of this equipment. A direct determination of sodium sulfate and sodium carbonate concentration in black liquor samples requires instrumental or analytical techniques that may be too expensive, too long or both. This work aims at a physical characterization of black liquor samples from the evaporation unit process streams, trying to establish a relation between some physical properties (density, viscosity and total solids content, which are easier to measure) and the concentration of sodium sulfate. Experimental data of this work have shown good reproducibility, and may be used to obtain a correlation between the physical properties measured and sodium sulfate content, allowing future studies that may lead to a better understanding of scaling formation process.

INTRODUCTION

In pulp and paper kraft mills, wood pulp is produced by digestion of wood chips in an aqueous solution containing sodium hydroxide and sodium sulfide - named white liquor, under high temperature and pressure. A by-product liquid stream of this digestion process known as weak black liquor, which has solids content of 15 wt% to 18 wt%, needs to be concentrated to higher solids content for its use as fuel in

the recovery boiler. To raise this concentration, a traditional multiple effect evaporators unit is used, resulting in a strong black liquor stream, usually with solids content in the range of 65 wt% to 75 wt%.

Inorganic compounds present in black liquor consist mainly of sodium salts and small amounts of potassium, calcium, magnesium, silicon and iron salts. Hendrick and Kent (1992); Rosier (1997); Adams (2001); Frederick Jr. (2004) and Soemardji (2004) have identified that solubility of sodium and potassium salts in black liquor is greater than others inorganic compounds, and that sodium salts are completely dissolved in the aqueous solution when solids content is less than 50 wt%.

During the evaporation process - when black liquors streams have a solid concentration above 50 wt%, sodium salts (Na_2SO_4 and Na_2CO_3) present in the black liquor reach their combined solubility limit, saturate and then begin to precipitate. The first salt that precipitates is usually the double salt burkeite, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. The scale formed by the deposition of this double salt is one of the greatest responsible for fouling problems in evaporators, resulting in efficiency loss of this equipment. This kind of scale is referred to as "soluble" scale, since these salts are soluble in water, which can be used to remove scaling from tubes in evaporators through a hydro-jetting process (Frederick Jr. , 2004).

Scaling by Na_2SO_4 - Na_2CO_3 double salts is a critical problem in black liquor evaporators since their deposition on heat transfer surfaces generates a scale insulating layer, causing quickly dropping of the heat transfer rate, forcing the evaporator to be shut down for cleaning (Gourdon, 2008). This means that black liquor evaporators are still a major bottleneck to improve pulp mill operational efficiency,

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especially when attempts to produce black liquor with solids contents as high as 80 wt% on a continuous base are made (Smith and Hsieh, 2000).

Some studies were performed attempting to simulate and predict scale formation in evaporators. In 1998 Golike have used NAELS (*Non-ideal Aqueous Electrolyte Simulator*) to obtain the solubility of inorganic compounds in black liquor, particularly sodium sulfate and sodium carbonate. Schmidl (2003) have presented solubility data for these same salts in aqueous solutions and in black liquor using batch evaporators, comparing the obtained results to the predicted solubility behavior by the use of a proprietary chemical equilibrium model. Soemardji (2004) developed a study aimed at understanding the crystallization process during black liquor evaporation, predicting crystal species transition in aqueous solution of Na_2CO_3 and Na_2SO_4 and in black liquor samples. Bialik (2007) have applied a thermodynamically-based model for predicting the solubility and solid-phase composition for burkeite precipitates, and this model was also used in an attempt to represent the solubility behavior in high temperature Na_2CO_3 - Na_2SO_4 solutions containing an additional anion.

There are also some experimental works involving laboratory or pilot scales facilities where sodium salts scaling was evaluated. Smith and Hsieh (2000) used both: a tube and a plate falling film evaporator to quantify the effects of operational and compositional variables to assist in scaling reduction. Euhus (2002) conducted studies in a falling film pilot evaporator to evaluate the effect of chemical composition and process variables on the rate of fouling at the heat transfer surface using salt aqueous solutions and black liquor. Bayuadri (2006) performed laboratory-scale evaporative crystallization experiments as close as possible to industrial process conditions, trying to investigate the stability of sodium sulfate dicarbonate (burkeite) crystals. Gourdon (2008) investigated the scaling behavior in a falling film evaporator trying to find favorable operating conditions to significantly decrease scaling, examining different heat flux, circulation flow rate, internal residence time and black liquor feed concentration.

Despite the many works on this matter, still there is a lack of data dealing with eucalyptus black liquor studies, since the majority of works offered by the literature refers to studies on pine black liquor. Only few papers related to researches on eucalyptus black liquor in association with the evaporation plant were found in the literature.

Koh and Lindberg (1999) reported developments in black liquor evaporation technology applied from pre-evaporation to super concentration of softwood and hardwood black

liquors, including eucalyptus black liquor. Ferreira (2003) have studied black liquor viscosity reduction by thermal treatment, evaluating the efficiency of this method. Ferreira (2004) evaluated the effect of the thermal treatment with an addition of salts aiming at reducing black liquor viscosity, and the obtained results showed this procedure can promote an appreciable reduction in viscosity. Gonçalves (2004) presented an analysis of composition and characteristics of kraft black liquor of Brazilian mills. Their work consisted on experimental determination of the liquor chemical composition by elemental analysis, and the determination of the main parameters that influence its viscosity. Cardoso (2006) have evaluated the influence of black liquor chemical composition on its physical properties, trying to predict its behavior in the recovery unit. They made use of samples from five different Brazilian mills and developed an experimental methodology to correlate elemental composition with physical properties. Cardoso (2009) have analyzed the effects of black liquor properties on its recovery unit, characterizing the main chemical and physical properties of eucalyptus kraft and bamboo soda black liquors with samples collected in six Brazilian mills.

Considering the existing lack of information about eucalyptus black liquor and that inorganic salt scaling in evaporators persists in being one of the most persistent operational problems in the pulp and paper industry, the aim of this work is to characterize eucalyptus black liquor samples by the determination of solids content, sodium sulfate content, density and viscosity; by evaluating the reproducibility of the obtained results with the applied techniques. The determination of sodium sulfate content in eucalyptus black liquor samples is of great importance not only because there are no many data in the literature about this property, but also because it is needed for a better understanding of the scale formation process in evaporators. The works of Cardoso (2006 and 2009) have provided a large set of data on many properties, e.g. density, heat power, specific heat and viscosity, which are related to the elemental analysis of the black liquor samples and some operational parameters, but it was not measured the concentration of the sodium sulfate itself. In this context, data presented in this work may be a contribution for future studies about eucalyptus black liquor scaling in evaporators.

MATERIALS AND METHODS

In this work, 13 sets of black liquor samples were collected at the evaporation plant of an industrial mill recovery unit. Each set contains samples of three different process streams: evaporation plant inlet stream (EPI); 6th effect recirculation stream (6ER)

Table 1. Experimental techniques used in the characterization of eucalyptus black liquor

Property	Techniques and equipments	Technique references
Viscosity (η)	Measurements of viscosity taken under different spindle rotational speeds at constant temperature – analog Brookfield viscometer, model LV	Brookfield Operator Manual and ASTM D-2196 (1991)
Density (ρ)	Gravimetric technique using specific gravity bottles (picnometers) and precision analytical balance ($\pm 10^{-4}$ g)	Costa <i>et al.</i> (1999)
Solids content	Drying of a determined mass of black liquor sample in an electric oven under controlled temperature until constant mass	TAPPI T650 cm-99 "Solids Content of Black Liquor" Method
Sodium sulfate content	Indirect determination by calculating barium sulfate content in a black liquor sample after physical and chemical treatment	TAPPI T625 cm-85 "Analysis of Soda and Sulfate Black Liquor" Method

and 2nd effect outlet stream (2EO). The choice of these process streams for analyses was defined in accordance with the process engineers of the industrial mill, who considered them as the most important for evaluation in this study. All samples were collected with stabilized process and operation in steady conditions, and then stored under refrigeration at 277.15 K until the beginning of the analysis procedures. Triplicate tests of each sample were performed, resulting in a total of 117 data for each property (13 sets of 3 process streams, repeated 3 times).

Equipments for the physical characterization of eucalyptus black liquor samples are: magnetic stirrer (Nova Ética/114); pH meter (Bel/103D); heating mantle (Fisatom/300); vacuum pump (Primatec/131); porcelain crucible (Chiarotti/B36); electric oven (Nova Ética/402N); muffle furnace (Fornitec/1900); desiccators (Chiarotti/280); electronic analytical balance (Bioprecisa/Fa 2104n); picnometer 50 mL (Vibrolabor); water bath (Nova Ética/500-3D); analog viscometer (Brookfield/LV); Petri dish (Schott 100x15 mm). The main reagents used in the experimental procedures were: HCl (Synth, P.A.); NH₄OH (Synth, P.A.); BaCl₂ (Dinâmica, 99% purity at 1.0 Molal) and distilled water.

Viscosities of all samples were measured with a Brookfield LV viscometer using the LV cylindrical spindles set for 2EO samples, and an ultra low (UL) adapter for EPI and 6ER samples. This UL adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube, and its cylindrical geometry provides extremely accurate viscosity measurements and shear rate determinations, being adequate for low viscosity measurements. For the 2EO samples, which have the highest solids content, spindle 63 has proved to be

the best for an accurate viscosity determination after three other spindles (61, 62 and 64) had been tested. The adopted experimental procedure is same as described by Li (1992).

Apparent viscosity at eight different spindle rotational speeds (0.3 to 60 rpm) are calculated in mPa.s (or centipoises) multiplying a scale factor (related to the shear rate) supplied with the viscometer by the scale reading of viscometer (related to the torque, and so, to the shear stress). Viscosity data were obtained at 293.15 K. This experimental procedure follows the ASTM D 2196 Method (ASTM, 1991).

RESULTS AND DISCUSSION

As already mentioned, thirteen sets of industrial black liquor samples collected in different days with process operating in steady conditions were analyzed, and three experimental runs were performed for each sample to check data reproducibility.

Table 2 shows experimental data for all the experimentally measured properties: sodium sulfate content, solids content, density and viscosity at spindle rotational. Considering the three experimental runs made for each set of samples, it is possible to infer that all data of the same set present a good reproducibility. When comparing different sets, there is also good reproducibility, and deviations from the mean value of the process stream are not greater than 20%, and may be attributed more to process fluctuations between the days that samples were collected at the mill than to uncertainties in the experimental procedure. Deviations of this order of magnitude are acceptable considering the experimental technique used and the process characteristics.

Table 2. Sodium sulfate content (SSC), solids contents (SC), density (ρ) and viscosity (η) at 60 rpm spindle rotational speed in eucalyptus black liquor samples

Set	Run #	SSC (kg/m ³)			SC (wt%)			ρ (kg/m ³)			η (mPa.s) at 60 rpm		
		EPI	6ER	2EO	EPI	6ER	2EO	EPI	6ER	2EO	EPI	6ER	2EO
1	1	2.6	5.0	6.9	15.3	26.0	38.7	1086.1	1164.0	1227.9	2.9	10.8	1000.0
	2	2.6	5.0	6.9	15.3	26.0	38.7	1086.5	1164.1	1228.7	2.9	10.9	1125.0
	3	2.7	5.1	6.9	15.3	26.0	38.8	1086.6	1164.5	1228.9	3.0	10.9	1187.0
2	1	2.6	4.2	7.4	15.8	23.4	40.5	1087.0	1131.5	1243.6	3.1	8.6	1237.0
	2	2.6	4.3	7.4	15.8	23.4	40.5	1087.2	1131.8	1243.8	3.1	8.6	1261.0
	3	2.7	4.3	7.4	15.8	23.5	40.6	1087.7	1131.8	1244.3	3.1	8.7	1354.0
3	1	2.4	4.8	7.1	14.7	26.1	40.3	1081.8	1169.2	1243.0	2.8	10.5	1186.0
	2	2.5	4.8	7.1	14.7	26.1	40.3	1082.2	1169.2	1243.3	2.8	10.5	1289.0
	3	2.5	4.9	7.3	14.7	26.2	40.3	1082.3	1169.5	1243.6	2.8	10.5	1308.0
4	1	2.5	4.4	7.0	15.2	23.7	39.5	1085.9	1135.0	1237.1	2.9	8.6	1127.0
	2	2.6	4.5	7.0	15.2	23.7	39.5	1086.0	1135.2	1237.1	2.9	8.7	1140.0
	3	2.6	4.6	7.1	15.3	23.8	39.6	1086.4	1135.4	1237.4	2.9	8.7	1288.0
5	1	2.6	4.5	6.9	15.1	23.9	39.4	1085.4	1139.3	1235.3	2.9	8.9	1152.0
	2	2.6	4.5	7.0	15.2	24.0	39.4	1085.8	1139.5	1235.4	2.9	8.9	1171.0
	3	2.6	4.6	7.0	15.2	24.0	39.4	1085.9	1139.7	1235.5	2.9	9.1	1187.0
6	1	2.5	4.2	6.6	14.8	23.0	38.1	1083.6	1129.3	1220.3	2.8	8.0	1028.0
	2	2.5	4.2	6.6	14.9	23.0	38.1	1083.7	1129.3	1221.2	2.9	8.0	1059.0
	3	2.5	4.2	6.7	15.0	23.1	38.2	1084.1	1129.6	1221.5	2.9	8.1	1144.0
7	1	2.8	4.3	6.7	15.9	23.5	37.9	1085.7	1132.3	1218.5	3.0	8.6	975.0
	2	2.8	4.3	6.8	15.9	23.5	38.0	1085.8	1132.4	1218.8	3.1	8.7	979.0
	3	2.8	4.3	6.8	16.0	23.6	38.0	1094.0	1133.1	1218.8	3.2	8.7	1013.0
8	1	2.6	4.3	6.8	15.1	24.0	37.5	1085.4	1139.0	1213.2	2.8	8.8	922.0
	2	2.6	4.4	6.9	15.2	24.0	37.5	1085.5	1139.3	1213.7	2.9	8.8	977.0
	3	2.7	4.5	6.9	15.2	24.0	37.6	1085.9	1139.3	1213.9	2.9	9.0	984.0
9	1	2.7	4.5	7.1	15.7	24.8	39.0	1086.6	1148.1	1233.4	2.9	9.1	1106.0
	2	2.7	4.6	7.2	15.7	24.8	39.1	1087.0	1148.3	1233.4	3.0	9.2	1149.0
	3	2.8	4.7	7.2	15.7	24.9	39.1	1087.1	1148.5	1233.7	3.0	9.2	1171.0
10	1	2.1	4.3	7.2	13.1	22.7	39.6	1070.2	1127.0	1239.5	2.6	7.6	1182.0
	2	2.1	4.3	7.3	13.1	22.8	39.6	1070.5	1127.4	1239.5	2.7	7.6	1186.0
	3	2.2	4.4	7.3	13.2	22.8	39.7	1070.5	1127.5	1239.8	2.7	7.7	1247.0
11	1	2.3	4.8	7.6	14.3	25.1	43.5	1080.2	1157.7	1251.5	2.7	7.7	1512.0
	2	2.4	4.8	7.7	14.3	25.1	43.6	1080.4	1158.2	1251.8	2.8	7.8	1534.0
	3	2.5	4.9	7.7	14.4	25.2	43.6	1080.9	1158.4	1251.8	2.9	7.9	1664.0
12	1	2.7	4.6	6.8	15.7	24.7	38.5	1086.8	1146.2	1223.5	3.0	8.9	1029.0
	2	2.8	4.6	6.8	15.7	24.8	38.5	1087.1	1146.6	1223.6	3.0	9.0	1128.0
	3	2.8	4.6	6.9	15.7	24.8	38.6	1087.1	1146.7	1224.3	3.1	9.1	1137.0
13	1	2.6	5.0	6.9	15.3	26.0	38.7	1086.1	1164.0	1227.9	2.9	10.8	1000.0
	2	2.6	5.0	6.9	15.3	26.0	38.7	1086.5	1164.1	1228.7	2.9	10.9	1125.0
	3	2.7	5.1	6.9	15.3	26.0	38.8	1086.6	1164.5	1228.9	3.0	10.9	1187.0

EPI = evaporation plant inlet stream; 6ER = 6th effect recirculation stream; 2EO = 2nd effect outlet stream

Results presented in Table 2 for sodium sulfate content analyses have shown good reproducibility, especially for EPI and 6ER samples. This is also observed for solids content and density. In the studied industrial process, nominal value for solids content in each process stream is: 15 wt% for EPI, 29 wt% for 6ER and 39 wt% for 2EO, and the obtained experimental results have proven good agreement with these three values (see **Table 3**). As expected, as long as solids content increases, values of other properties also increase.

Data dispersion in physical properties is greater for the 2EO samples due to difficulties in doing their analyses, that because at high solids concentration the samples manipulation and the application of the used techniques is a quite hard task. Especially for viscosity measurements, data have shown a great dispersion because samples from this process stream are non uniform, and results depend not only on the technique used, but also on the process conditions. Table 3 presents mean values and standard deviation obtained for all the properties measured in this work.

It was observed that at 293.15 K and low concentrations (around 30 wt% of solids content), eucalyptus black liquor behaves like a Newtonian fluid, in agreement with the results related by Ferreira (2003), Ferreira (2004) and Gonçalves (2004). According to Cardoso (2009) the chemical composition of black liquor - basically the amount of polymeric organic matter (lignin and polysaccharides) and of inorganic compounds, directly influences the density and viscosity. At high shear rates, lignin macromolecules tend to align together, reducing their resistance to flow, and so the liquor viscosity.

For black liquor samples with high solids concentrations (above 30 wt%) it was observed that a great decrease in

viscosity value occurred when an increase in spindle rotational speed was applied, implying that viscosity decreases as shear rate increases. This behavior identifies that black liquor in 2EO process stream is a viscous pseudoplastic fluid, once again in agreement with the observations of previous works.

CONCLUSION

The results presented in this paper have proved good reproducibility, confirming that all experimental techniques applied are adequate to get the necessary data for future study, looking forward for a better understanding of scale formation process, trying to link this phenomenon to the black liquor physical properties, especially sodium salts content.

Physical properties of black liquor may vary considerably due to chemical composition associated with the type of processed wood and operational conditions of the pulping phase. Therefore, the greater the amount of experimental data on eucalyptus black liquor physical properties, the better the comprehension whether these properties may be somehow correlated and in which way they can be used to understand scale formation in evaporators, and how to prevent or even avoid this problem by accompanying the variation of the considered properties. Data presented in this work may well contribute to this intent.

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Table 3. Mean and standard deviation for physical properties in each process stream

Process stream	Solids content (wt%)	Density (kg/m ³)	Viscosity* (mPa.s)	Sodium sulfate content (kg/m ³)
EPI	15.14 ± 0.76	1084.55 ± 4.87	2.92 ± 0.13	2.59 ± 0.19
6ER	24.34 ± 1.05	1144.83 ± 13.95	8.97 ± 0.94	4.56 ± 0.26
2EO	39.56 ± 1.56	1233.69 ± 11.53	1187.46 ± 167.09	7.17 ± 0.52

* for spindle rotational speed set at 60 rpm

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