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Investigation of Thermal Analysis Techniques Potential to Determine Solids Content in Eucalyptus Black Liquor Samples

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In pulp and paper mills, the aqueous solution extracted from the pulping process in the wood digester is called black liquor, which consists of organic and inorganic compounds. When leaving the digester sector, black liquor has about 15 wt% of solids and to be used as a fuel in the recovery boiler it is necessary to raise this solids content to 75 wt%, removing water in a battery of multiple effect evaporators.
Some black liquor physical properties, such as, salt contents and boiling point rise (BPR), are strongly dependent on the kind of wood processed (hardwood or softwood) and on operational conditions during the digestion process. Knowledge and comprehension of the relationship between these physical properties of black liquor are essential for studies aiming at a greater energetic performance of the black liquor evaporation unit.
The continuous increasing of the production rate of pulp and paper mills around the world also causes an increasing of black liquor production, and then the concentration process of this liquor may represent a bottlenecking problem when operational problems arise from scaling formation in evaporators.
The concentration of solids in black liquor above 75 wt% causes scaling formation on the heat transfer surfaces of evaporators and concentrators, due to precipitation of sodium salts, reducing the overall efficiency of this equipment.
The aim of this work is to evaluate the potential of some traditional thermal analyses techniques, TG and DSC, as alternative methods to estimate solids content in eucalyptus black liquor, since this information is essential to understand scaling formation process. These alternative methods may represent a faster and safer option when compared with conventional gravimetric methods.
The results have shown that it is possible to use these alternative techniques to obtain fine and accurate results, but it is important to observe that the cost-benefit relationship of the traditional technique is much greater. This work represents an important contribution since there are not many works in the literature dealing with the use of these techniques for eucalyptus black liquor samples.

1. Introduction

In traditional pulp and paper Kraft mills the industrial process may be divided in two sections: fibers and chemical recovery. The first one extends from the wood digester to the pulp bleaching section, passing

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by the brown pulp washing step. The main goal of the this section is to remove lignin from wood producing a pulp with a high whiteness at the end of the bleaching sequence. A by-product aqueous solution stream of the wood digestion process, known as weak black liquor, has about 15 wt% of solids and needs to be concentrated to a higher solids content (75 wt%) to be used as fuel in the recovery boiler. The second section, named chemical recovery, involves a multiple effect evaporators unit, the recovery boiler and the causticizing sector. This process is necessary to make the pulping process economically feasible, incinerating black liquor to produce high pressure steam in the recovery boiler and recycling inorganic chemicals to the process.

Scaling formation in black liquor evaporators is a serious problem which reduces the efficiency and the production capacity of this equipment. This happens because salt deposition on tube walls produces an insulating layer of scales which quickly reduces heat transfer rate and forces the evaporator to be shut down for cleaning. In some cases these tubes may also be obstructed, leading to emergency stops for maintenance (Gourdon et al., 2008). This problem occurs when black liquor solids content is higher than 45 wt%, because the solubility limit of sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4) is reached. When Na_2CO_3 and Na_2SO_4 form the double salt burkeite ($2Na_2SO_4.Na_2CO_3$) it precipitates on the equipment walls forming a scaling deposit (Hendrick et al., 1992; Rosier, 1997; Adams, 2001; Frederick et al., 2004; Soemardji et al., 2004).

A continuous increasing of the production rate of pulp and paper mills around the world also causes an increase of black liquor production and then the concentration process of this liquor may represent a bottlenecking problem when operational problems arise from scaling formation in evaporators. Cleaning evaporators tubes prevents the build-up of scaling on the heat transfer surfaces, however this process, usually done by hydro jetting, can become ineffective since it is normally carried out in fixed time periods, generally without any investigation on the evolution of the real conditions at the evaporator surface. This scaling formation becomes greater especially when attempts to produce black liquor with solids contents higher than 80 wt% are made (Smith and Hsieh, 2008).

Considering this critical problem, a better understanding of the precipitation/incrustation process can be accomplished by analysing solid and salt contents in black liquor, which is an essential information to comprehend this phenomenon. The determination of solids and sodium sulphate content by a gravimetric method is quite simple and allows fine results. Nevertheless, this technique requires experimental runs that take a long time (about 36 h). The main advantage of using alternative methods like TG (thermogravimetry) and DSC (differential scanning calorimetry) is that these methods allow quick results (approximately 20 min) with great accuracy, and this can be crucial when the process demands actions in a short time to avoid operational problems (Mullin, 2001).

Therefore the aim of this work is to evaluate the applicability of thermal analysis techniques - TG and DSC – as alternative methods to determine total solids content and sodium sulphate concentration in industrial eucalyptus black liquor samples, since this information is essential to understand scaling formation process. These alternative methods may represent a faster and safer option when compared with conventional gravimetric methods. The results obtained with these alternative techniques will be compared with the traditional ones obtained by standard technique TAPPI T650 om-09.

2. Experimental

2.1 Black liquor samples

In this work, industrial samples of eucalyptus black liquor were collected in three different process streams in the evaporation plant of a Brazilian Kraft mill. These process streams are identified as: evaporation plant input stream (EPI); 6^{th} effect recirculation stream (6ER) and 2^{nd} effect output stream (2EO), as shown in Figure 1. The choice of these process streams to be analyzed was defined based on the opinion of the process engineers of the industrial mill, who considered them as the most important ones to be studied. All samples were collected when the process was stabilized, operating at steady state conditions and then stored under refrigeration at 277.15 K (4 °C) until the beginning of experimental analyses procedures. Industrial nominal values for solids content in each process stream are: 15 wt% for EPI, 30 wt% for 6ER and 45 wt% for 2EO.

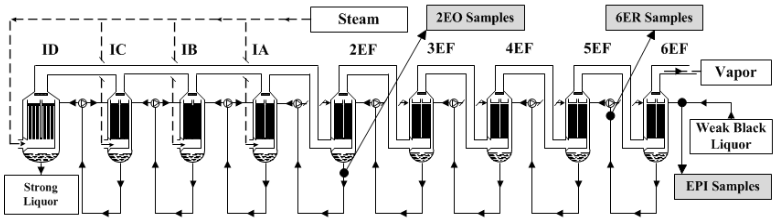

Figure 1: Flowchart of the industrial evaporation unit

2.2 Dry solids content – gravimetric method

Dry solids content is defined as the ratio between black liquor mass after thermal treatment and the initial mass of the sample. A traditional technique used to determine dry solids content is based on TAPPI T650 om-09. The experimental steps are: pre-dry Petri dishes by placing then in a drying oven heated at 378.15 K (105 ^oC) for 2 h; after that, remove the dishes from the oven, cooling them in a desiccators; weight this pre-dried dish using an analytical balance and record its mass. Weight 15 g of a black liquor sample and record the weight of this sample plus the weight of the dish. Place the sample in the Petri dish and put them inside the oven at 378.15 K (105 ^oC) for 24 h. Remove the sample from the oven and allow it to cool to room temperature in a desiccators. Weight the dish containing the oven-dried sample and record this mass. Place the sample back into the oven again for more 12 h. Remove the sample from the oven and allow it to cool to room temperature in a desiccators, measuring its mass again. Repeat these last steps until obtain a constant mass for the set (sample plus Petri dish). Once the sample has been dried to constant mass, solids content may be calculate, using the relation between the final and initial mass of the sample (Torniainem, 2001; Cardoso et al., 2009). Equipment used: analytical balance from Metler, model AB204 (uncertainty ± 10^{-4} g) and electric oven from Nova Ética, model 402N.

2.3 Thermogravimetric analyses

TG curves were performed in a Thermogravimetric Analyzer Model TGA 2050 Thermobalance using a heating rate of 10 $K.min^{-1}$, with nitrogen (flow rate: 55 $cm^3.min^{-1}$) in the temperature range from 298.15 K to 573.15 K (25 °C to 300 °C). Black liquor samples (5.00 ± 0.5 mg) were placed on a platinum pan. At the end of the experimental running a TG curve was obtained showing the thermal effects occurred in the samples. The TG instrument was calibrated using calcium oxalate monohydrate.

2.4 Differential scanning calorimetry

DSC curves were performed using a TA Instruments Model DSC 2020 Modulated DSC. Experimental parameters were defined as: heating rate of 10 $K.min^{-1}$, in nitrogen (flow rate 70 $cm^3.min^{-1}$) and temperature range from 298.15 K to 523.15 K (25 °C to 250 °C). Black liquor samples (2.00 ± 0.2 mg) were put into an aluminum sample holder and then the cell was sealed hermetically. Temperature and heat flow of the DSC instrument were calibrated using the melting point and enthalpy of fusion of standards components (indium and zinc).

2.5 Sodium Sulphate Content

Gravimetric analysis was performed according to TAPPI T 625 cm-85 (Tappi,1985). Black liquor samples were neutralized with hydrochloric acid (HCl), the mixture is then warmed, cooled and filtered. Solids retained are washed, neutralized with NH_4OH, boiled and $BaCl_2$ is added. Sulphate precipitates as barium sulphate ($BaSO_4$) after reacting the samples with barium chloride. $BaSO_4$ formed was ignited in an muffle furnace (Fornitec, model 1900) at 800 °C, cooled, and weighed.

3. Results and discussion

Experimental data for solids contents in black liquor samples, obtained by a traditional technique (TAPPI 650 om-09) when the industrial process was stabilized and operating at steady state conditions, were taken from Andreuccetti et al. (2011). Table 1 shows the results for solids content in black liquor samples, obtained from both experimental methods: traditional (gravimetry) and alternative (thermal analysis – TG and DSC), presenting average values and standard deviations.

Table 1: Experimental values (wt% of solids content) in black liquor samples with their respective standard deviations

Process Stream	Experimental technique	
	Traditional	TG
EPI	16.38 ± 0.82	18.35 ± 0.38
6ER	31.86 ± 1.85	30.78 ± 0.12
2EO	49.12 ± 0.59	47.28 ± 0.52

As summarized in Table 1, the results of dry solids supplied by thermal analyses are in good agreement with those obtained using the traditional technique and are also coherent with the nominal value of the industrial process from where the samples were collected.
Three TG curves obtained for one set of black liquor samples (EPI, 6ER and 2EO) are shown in Figure 2, which allows the observation of mass loss events between 303.15 K and 423.15 K (30 °C and 150 ºC), which are due to water evaporation. According to TG profiles all black liquor samples have presented the same behavior, independently of dry solids concentration.

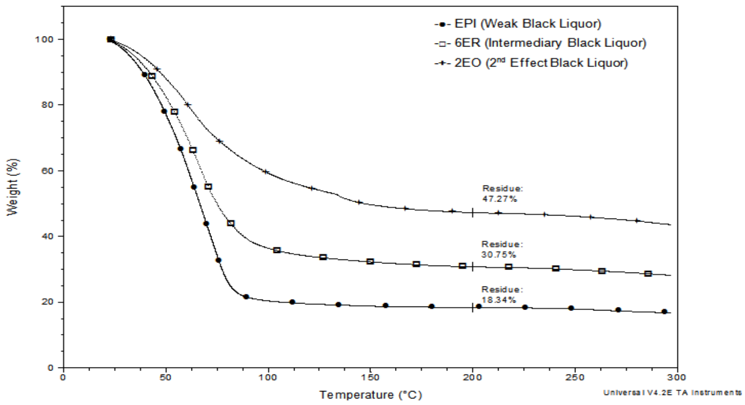

Figure 2: TG curves of black liquor samples for a heating rate of 10 K.min^{-1}

In Figure 2 it is also observed that the main difference between the curves of EPI, 6ER and 2EO samples is the temperature range in which the event of evaporation occurs. This temperature range results from the difficulty towards the evaporation that is proportional to the increasing of solids content in black liquor. Mass loss events from the samples of the EPI stream occurred between 363.15 K and 373.15 K (90 °C and 100 °C), for 6ER stream between 373.15 K and 383.15 K (100 °C and 110 °C) and for 2EO stream between 411.15 K and 421.15 K (138 °C and 148 °C).
Furthermore, considering the temperature range of the experimental run (30 ºC to 300 ºC), events related to thermal degradation were not observed for all samples studied. According to the literature, events which characterize thermal degradation or other mass losses might occur in temperatures higher than 573.15 K (300 ºC) (Bartkowiak and Zakrzewski, 2004; Loung et al., 2012).
Interpretation of the curves presented in Figure 2 also points out that 2EO samples have a lower water content compared with EPI and 6ER stream samples and that EPI samples has the highest water content compared with the others. These results were expected since the concentration of dry solids increased in the following order: 2EO (Δm = 47.27 wt%) > 6ER (Δm = 30.75 wt%) > EPI (Δm = 18.34 wt%).
Black liquor samples were also investigated by DSC experimental technique whose curves obtained are presented in Figure 3. From the DSC technique it is possible to identify the kind of mass loss

events explained in the TG analyses. In principle, Figure 2 shows a tendency of an endothermic peak for all the samples in the temperature range from 303.15 K to 373.15 K (30 °C to 100 ºC).

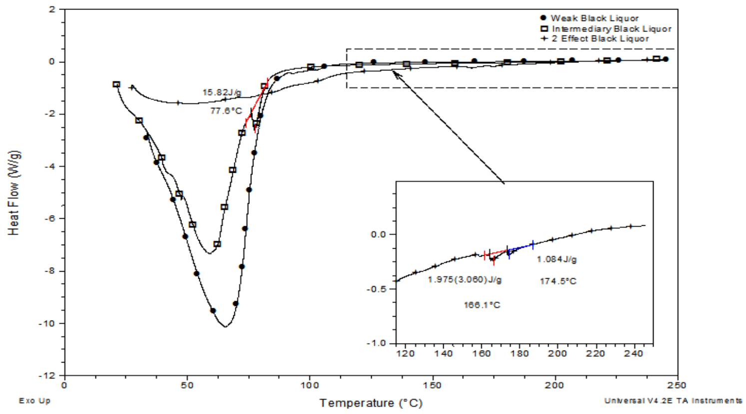

Figure 3: DSC curves of black liquor samples

This endothermic peak corresponds to water desolvation which is in good agreement with the results of water losses in the TG curves, as related in previous works (Venkatesh and Nguyen, 1985; Adams et al., 1997). An individual analysis of DSC curves in Figure 3 shows that there is no additional events in weak black liquor sample (EPI). This is expected because for black liquor with low solids concentration, around 15 wt%, all salts present are soluble. For the intermediary black liquor sample (6ER) and 2nd effect black liquor sample (2EO) small peaks are observed, which may be interpreted as a reduction of salts complexation. This phenomenon in black liquor is expected, which leads to scaling formation in evaporators tubes (Adams, 2001).

As shown in Figures 2 and 3, in the range of solids content between 18 to 45 wt%, the salts present are completely soluble in black liquor, although they may precipitate at any system perturbation. Equation 1 was developed based on a regression of 22 sets of experimental data, and can be used to predict sodium sulphate content as a function of solids content in the range from 18 to 45 wt%.

$$C_{Na2SO4} = 0.2166SC - 0.2967 \quad (1)$$

C_{Na2SO4} is sodium sulphate content (in kg/m^3) and *SC* is solids content (in wt%) present in black liquor.

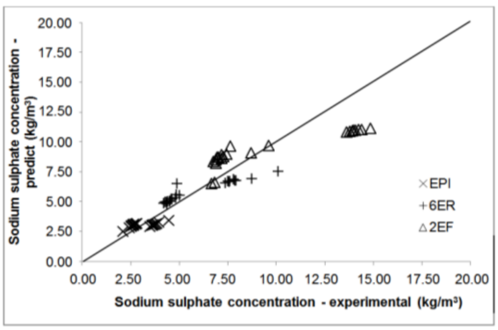

Figure 4: Comparison between experimental and predict values for the sodium sulphate content

Figure 4 shows a comparison between experimental data and the ones obtained by Eq. 1, showing that especially for samples of low sodium sulphate concentration, it is possible to obtain a good prediction.

4. Conclusion

In this work data for total solids content in eucalyptus black liquor samples, using thermal analyses (TG and DSC) were presented. Comparing these results with the ones obtained by traditional techniques it is possible to conclude that these alternative techniques are adequate, giving reliable results. Since sodium sulphate is one of the most important responsible for scaling formation in evaporators tubes and considering that the concentration of this salt is directly related with the concentration of total solids, a correlation of these two properties was proposed. The results obtained with this correlation have shown to be in good agreement with experimental data. This work consists of the first step of an investigation that is being developed about salts solubility in eucalyptus black liquor. The greater the understanding of scaling process formation the better the process will operate resulting in cost reduction and also an increasing in production efficiency.

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