

Vapor Pressure and Boiling Point Elevation of *Eucalyptus* Kraft Black Liquors

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Abstract. Vapor-liquid equilibria and boiling point elevation of eucalyptus kraft black liquors over a wide range of solid concentrations (up to 72% solids) has been studied. The liquors were prepared from original samples taken from the outlet of the evaporation plant of a Portuguese mill. It was found that boiling point elevation of black liquors is pressure and temperature dependent and this dependency is more significant at higher solids concentrations. The heat of vaporization is not strongly affected by solids content. The boiling point elevation data at different solids contents (at a fixed pressure) were correlated with the dissolved solids in black liquor. We have observed a change in the slope of the boiling point elevation as a function of the dissolved solids at nearly 43% solids.

Key words: Black liquor; vapor pressure; boiling point elevation; evaporation; *eucalyptus*

Pressão de Vapor e Elevação do Ponto de Ebulição do Licor Negro do Eucalipto

Sumário. Estudou-se o equilíbrio líquido-vapor e a elevação do ponto de ebulição do licor negro resultante do cozimento kraft de aparas de eucalipto, com teor de sólidos até 72% (em massa). Os licores foram preparados a partir de amostras recolhidas à saída da unidade de evaporadores de uma fábrica Portuguesa. Verificou-se que a elevação do ponto de ebulição dos licores negros é dependente da temperatura e pressão, e essa dependência é mais significativa para concentrações elevadas de sólidos. O calor de vaporização não varia muito com o teor de sólidos. Os valores da elevação do ponto de ebulição, para diferentes teores de sólidos a uma pressão fixa, foram correlacionados com os sólidos dissolvidos no licor negro. Para um valor próximo de 43% de teor de sólidos observou-se uma alteração no declive da elevação do ponto de ebulição em função do teor de sólidos dissolvidos.

Palavras-chave: Licor negro; pressão de vapor; elevação do ponto de ebulição; evaporação; *eucalyptus*

La Pression de la Vapeur et l'Élévation du Point d'Ébullition des Liqueurs Noires d'Eucalyptus

Résumé. L'équilibre liquide-vapeur et l'élévation du point d'ébullition des liqueurs noires d'eucalyptus (kraft) a été étudié sur une large gamme de concentrations de teneur en solides dissous (jusqu'à 72% de teneur en solides). Les liqueurs ont été préparées à partir d'échantillons recueillies après le procédé d'évaporation d'une usine portugaise. Nous avons constaté que l'élévation du point d'ébullition est dépendante de la pression et de la température et cette dépendance est plus importante à des taux de matières solides plus élevées. La chaleur de vaporisation n'est pas fortement affectée par la teneur en solides. Les valeurs de l'élévation du point d'ébullition (à une pression fixe) ont été corrélées avec la teneur en solides dissous dans la liqueur noire. Nous avons observé un changement dans la pente de l'élévation du point d'ébullition en fonction des solides dissous après la valeur de 43% de matières solides.

Mots clés: Liqueur noire; pression de vapeur; élévation du point d'ébullition; évaporation; *eucalyptus*

Introduction

Black liquor (BL) is the name applied to liquors recovered from the digesters up to the point of their incineration in the recovery plant. It consists of the remaining organic substances after the digestive process where the cellulose fibers have been cooked out from the wood and organic components in an alkaline aqueous medium.

The knowledge of black liquor vapor pressure (VP) and boiling point elevation (BPE) over wide ranges of temperature and solids concentrations is important for the development, design, and performance characteristics of evaporation equipment in the chemical recovery operations of the Kraft unit. These properties depend markedly on the solid concentrations (and liquor composition) (CLAY and GRACE, 1984; SZYMONSKI and GRACE, 1985; ZAMAN *et al.*, 1998). In modern kraft pulp mills the recovery boilers are plant burning BLs at very high solids content (79% solids and above), thereby improving efficiency by reducing the energy spent in drying BL droplets before combustion. The evaporators have to produce BL at increasing solids levels and the

evaluation of the VP and BPE at higher solids content (S) is of critical importance as more evaporation stages are needed to reach these limits.

Although some important investigations on the measurement techniques and data on VP and BPE for softwood BLs have been made (CLAY and GRACE, 1984; SZYMONSKI and GRACE, 1985; ZAMAN *et al.*, 1998), the data for hardwood, and specifically for Eucalyptus used in the Portuguese industrial pulpmaking processes, are scarce. In this work we report results on vapor-liquid equilibria (VLE) and BPE-concentration-temperature relations for Eucalyptus kraft BLs over a wide range of solids concentrations.

Several methods of measurement have been reported since 1939. The main problem is the difficulty to reach the equilibrium between the liquor and water and the superheating of liquor at higher solids concentrations. A good review and discussion of the techniques used can be found in the literature (ZAMAN *et al.*, 1998; STOY *et al.*, 1992).

The purpose of this research is to develop a consistent set of vapor pressure and boiling point rise data for Eucalyptus BLs. We are interested in the

following objectives: (i) the study of VLE and BPE with increasing solids content, especially at high concentrations where the solubility limit of some of BL components is exceeded; (ii) to develop quantitative models involving all the variables; and (iii) to optimize the instrumental techniques for measurement of VLE and BPE. The results of these tasks are presented below.

Experimental

Black liquor suspensions with different solids content were prepared from original samples taken from the outlet of the evaporation and concentration plant of a Portuguese mill. The composition of these samples and of the prepared ones is reported in Table 1. Black liquor solids content was measured using TAPPI method T650 OM-89. The samples BLSPA, BLSPB and BLSPC were used to measure the boiling point rise at atmospheric pressure using technique A. The liquors BLSPA and BLSPB were collected about one year before liquor BLSPC. Vapor-liquid equilibria and boiling point rise data were obtained using the samples BLSPD and BLSPE with technique B.

Figure 1 shows the apparatus used to measure BPE using technique A. The main part is a small stirred evaporator made of glass and operating at atmospheric pressure. The evaporator cell is heated by an electric blanket with three rates of heating. The evaporator was combined with a Graham condenser cooled by water and operating at total reflux. This system of condensation was selected because it presents an adequate area for heat transfer. The cooling water in the condenser comes from a thermostated HAAKE D8-G bath, being the flow controlled by a circulation pump. The temperature of the black liquor was measured using an immersion mercury thermometer graduated from 50 to 150°C, with a resolution of 0.1°C. The volume of black liquor used was 100 ml. The system was previously tested with tridistilled water to find the operating conditions that reduce overheating. We measured the normal boiling point in the presence of glass spheres, employed as boiling regulators, and using an intermediate heating rate. Experimental boiling point measurements agreed with literature values within $\pm 0.4^\circ\text{C}$.

Table 1 - Composition of original and prepared samples

Black Liquor	Original Samples Solids Content (%)	Prepared Samples Solids Content (%)	Technique
BLSPA	50	12.3, 18.9, 24.5, 30.6, 36.2, 41.4, 48.4, 61.4, 63.4	A
BLSPB	65	11.5, 15.6, 20.1, 25.5, 32.0, 37.7, 42.0, 47.3, 62.4, 62.7, 64.9, 66.9	A
BLSPC	72	10.0, 19.7, 29.2, 39.0, 49.7, 60.9, 64.9, 69.0, 72.3	A
BLSPD	70	19.8, 30.5, 39.4, 49.2	B
BLSPE	70	10.0, 24.0	B

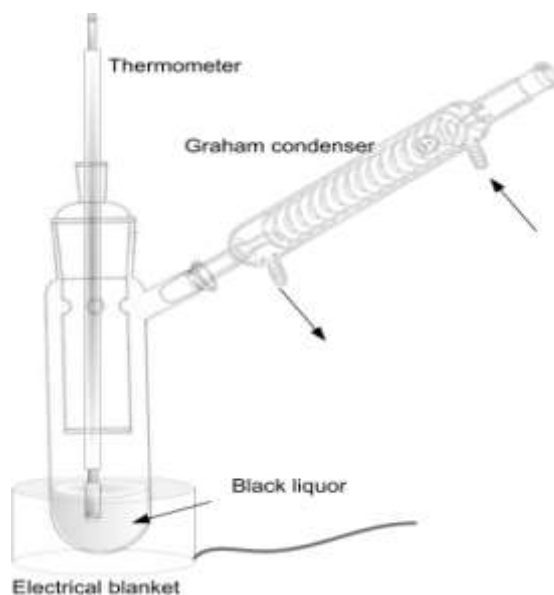


Figure 1 - Boiling point measuring system (A) for black liquor

Figure 2 shows the apparatus used to measure the vapor pressure (and boiling point rise) (Technique B). The glass cell (1) which is charged with roughly 500 ml of black liquor has a lid with three outputs: (i) for a Pt100 probe; (ii) to insert a Graham condenser that is connected to tap water; (iii) for insertion of a stirrer driven by a flexible cable connected to a multi-speed electric motor (5). The temperature of the vapor leaving the evaporator cell was measured using the Pt100 probe. At the upper end of the condenser there is a two way valve to release the non-condensable gases. This valve is also connected to a ballast (2). The pressure is read on a mercury manometer (3) fitted with a three-way valve at the end which allows connection to a vacuum pump (4) and can also be

opened to the atmosphere. The heating of the cell is provided by a copper cup where the evaporator cell was partly introduced and that in turn is attached to an HAAKE thermostatic bath. The facility is supported by a metal frame built for this purpose. The Pt100 probes were calibrated against standard certified thermometers and the uncertainty in temperature measurement is less than $\pm 0.1^\circ\text{C}$. The pressure reading was made with a cathetometer, obtaining an overall uncertainty of approximately ± 0.5 mm for that property. The system was previously tested with tridestilled water and sodium chloride solutions (STOY *et al.*, 1992). Experimental boiling point measurements agreed with literature values within $\pm 0.5^\circ\text{C}$.

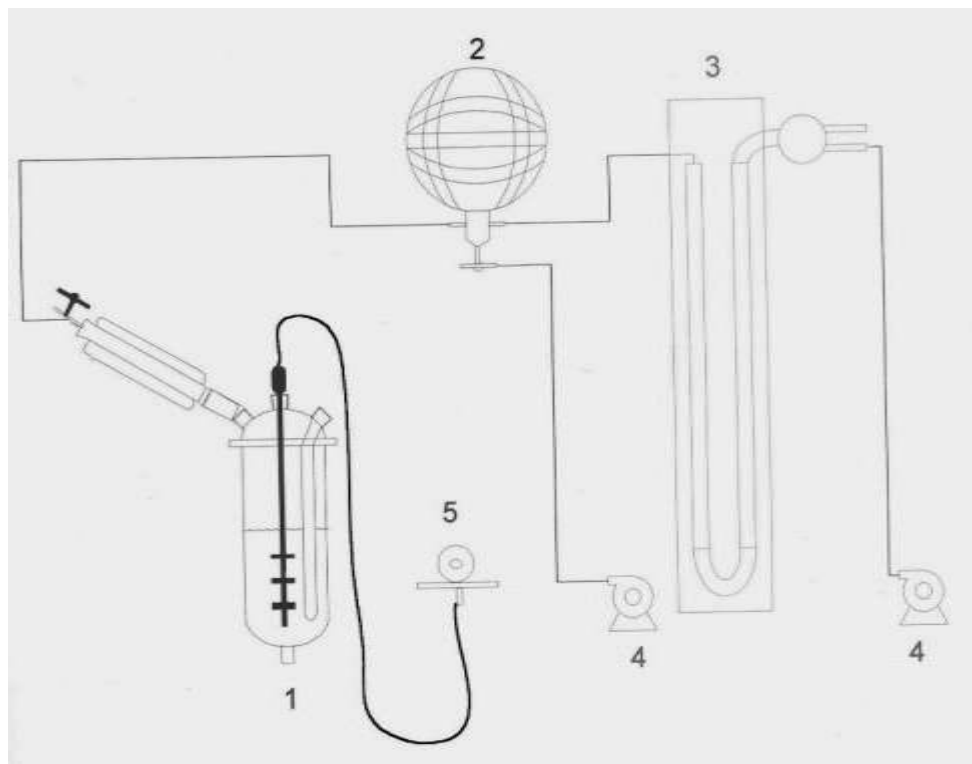


Figure 2 - Measuring system B for black liquor boiling point. Legend: 1. Glass cell; 2. Ballast; 3. Mercury manometer; 4. Vacuum pumps; 5. Multi-speed electric motor

Results and discussion

Vapor-liquid equilibria

The vapor pressure as a function of the temperature and the composition of black liquors BLSPD and BLSPE has been studied using the technique B. In Figure 3, we have plotted the vapor pressure as a function of temperature for concentrations from 20% to 50% solids content along with the vapor pressure of water. The vapor pressure decreases with the rise of solids content and its behavior when increasing temperature is virtually the same at all the concentrations.

It is important to note that we have removed the volatile organics before the vapor pressure measurements. The Wrede equation

$$\ln P = A - \frac{B}{T} \quad (1)$$

was applied, fitting successfully the experimental pressure and temperature (P , T) data as can be seen in Figure 3. If we treat BL as a binary solution (organic+inorganic components in water) at equilibrium conditions, where the liquor and the water vapor are at equilibrium with one another at temperature, T , and pressure, P , the Clapeyron equation applies:

$$\frac{dP}{dT} = \frac{\Delta_L^G H}{T \Delta_L^G V} \quad (2)$$

where $\Delta_L^G V$ is the increase in volume on vaporization, and $\Delta_L^G H$ is the enthalpy of vaporization.

If we assume that the vapor phase is a perfect gas and considering $\Delta_L^G H$ as constant, the integration of equation (2) gives equation (1), where $B = \Delta_L^G H / R$ and the calculation of $\Delta_L^G H$ follows from equation (1). The values of parameters A and B and the calculated heat of vaporization are given in Table 2. If the heat of vaporization was constant, there should not be any variation in the values of B , for a given liquor, when the concentration of solids changes.

For liquor BLSPD parameter B does not change appreciably, but its value is significantly different from the same parameter found for liquor BLSPE. Therefore, the enthalpy of vaporization shows small variations for liquor BLSPD and is much higher than the value found for BLSPE, which is close to this property reported for water. Apart from the experimental errors, the main factors causing the variation of B are the non-ideality nature of black liquor (STOY and FRICKE, 1994a; STOY and FRICKE, 1994b; ZAMAN and FRICKE, 1996; ZAMAN *et al.*, 1996) and the fact that the heat of mixing should not be ignored in evaporation measurements.

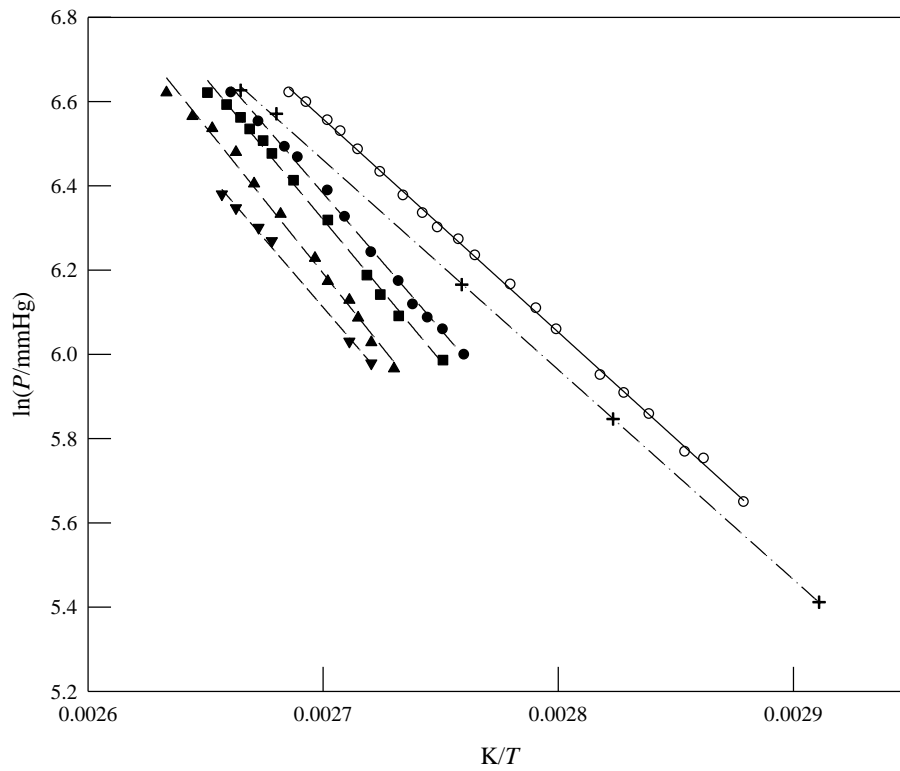


Figure 3 - Vapor pressure of black liquors, P , as a function of temperature, T , and solids content, S : (\circ) water; BLSPD: (\bullet) $S = 19.8\%$; (\blacksquare) $S = 30.5\%$; (\blacktriangle) $S = 39.4\%$; (\blacktriangledown) $S = 49.2\%$; BLSPE: ($+$) $S = 24.0\%$

Table 2 - Estimated parameters A, B and enthalpy of vaporization of equation (1), and related coefficients of correlation

Sample	S (%)	A	B (K)	$\Delta_L^G H$ (kJ mol ⁻¹)	R ²
BLSPD	19.8	23.85	6469.5	53.8	0.997
	30.5	24.45	6716.5	55.8	0.996
	39.4	25.02	6971.5	58.0	0.997
	49.2	23.67	6502.2	54.1	0.996
BLSPE	24.0	19.90	4979.0	41.4	0.998
Water	-	20.23	5062.2	42.1	0.999

Boiling point elevation

The boiling point elevation for black liquors is defined as the difference between the boiling point of black liquor solution and that of pure water at the same pressure. In Figure 4 we present the BPE as a function of solids content for liquors BLSPA, BLSPB, BLSPC and BLSPD at atmospheric pressure.

First it appears that the variation of BPE with the solids content of liquor for BLSPA, BLSPB and BLSPC is similar, even though the liquors were collected at a very different time. Although more tests will be needed, it can be concluded that the age of the liquor has little influence on this property. Second it can be observed that the BPE becomes greater as solids content raises: for concentrations below 30% the BPE does not increase significantly. The liquor BLSPD shows BPE values higher than those of other liquors, especially for upper concentrations of solids. The observed variations can be explained by differences in composition and by the fact that for liquor BLSPD, BPE values are calculated from the curves of vapor pressure by solving equation (1) in order to temperature.

If one considers that black liquor

solutions are binary mixtures, BPE can be described as a function of molality, m , as

$$\Delta T = K_m m \quad (3)$$

where K_m is a solvent dependent constant. As molality is proportional to the ratio solid / water equation (3) can be written as

$$\Delta T = K \frac{S}{100 - S} \quad (4)$$

For softwood black liquors equation (4) applies up to about 50% of solids (FREDERICK *et al.*, 1980).

In Figure 5 the dependency of ΔT on $S/(100-S)$ is shown. Parameter K ($=7.454$) was found by fitting BPE of liquors BLSPA, BLSPB and BLSPC. For higher concentrations, when S is greater than 43 %, a change in the slope of the straight line is observed resulting $\Delta T = 3.231 + 3.148 S$. Considering the individual behavior of each BL, the above referred change in the slope happens at 40%, 57% and 45% for the liquors BLSPA, BLSPB and BLSPC, respectively. This slope alteration is caused by the solubility limit of sodium sulphate and sodium carbonate in the liquor (FREDERICK *et al.*, 1980). During concentration of black liquor the salts of sodium begin to precipitate as Na_2SO_4 , Na_2CO_3 or their double salt (burkeite = $=2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), when their concentration exceeds the critical

concentration of the liquor (VAKKILAINEN, 2000). This precipitate can cause fouling in the evaporator, which is a costly phenomenon due to the energy losses, the higher maintenance and the break in production that occurs during shutdown for equipment cleaning. As a consequence to this precipitate salt formation in our measurements, the concentration of dissolved inorganic (Na_2SO_4 and Na_2CO_3) remains fairly constant, as S is increased, and the ratio $S/(100-S)$ augments more slowly above the clear change of slope. (as S is increased above the solubility limit of Na_2SO_4 and Na_2CO_3). However, the organics and other soluble inorganic do not

precipitate, and they account for the increase in BPE above the solubility limit of Na_2SO_4 and Na_2CO_3 . The behavior of a softwood (Slash pine) black liquor (ZAMAN *et al.*, 1998) as depicted in Figure 5, shows that burkeite precipitation occurs later, nearly at 64% of solids. Nevertheless, the initial slope is very similar to Eucalyptus (hardwood) and pine (softwood). This behavior can be explained by the fact that the burkeite precipitation can start at a critical concentration between 45% to 65% dry solids, being this solubility limit dependent on the dissolved wood species, the temperature, the ratio of CO_3 to SO_4 and the total effective Na content in black liquor (VAKKILAINEN, 2000).

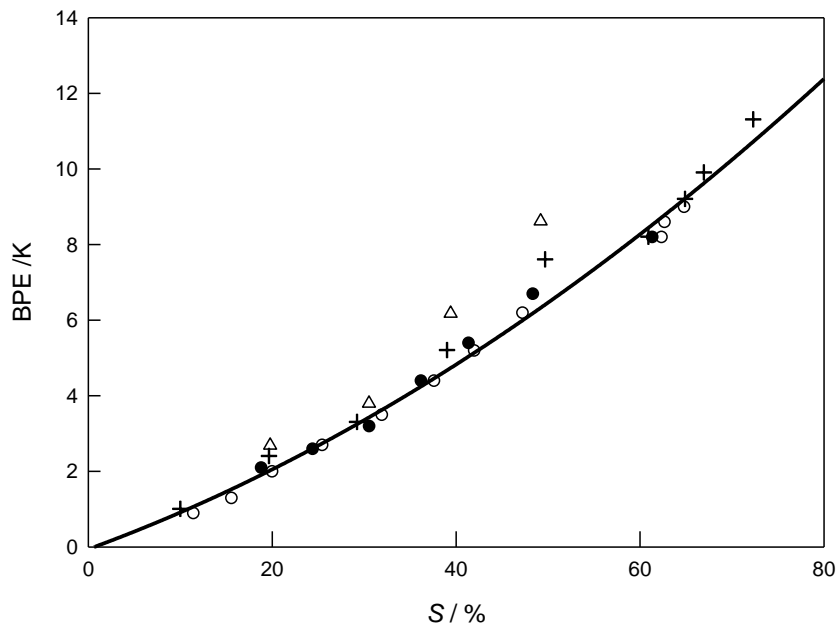


Figure 4 - Boiling point elevation, ΔT , as a function of solids content, S , at atmospheric pressure: (●) BLSPA; (○) BLSPB; (+) BLSPC and (Δ) BLSPD. The line represents the global behavior considering the liquors BLSPA, BLSPB and BLSPC

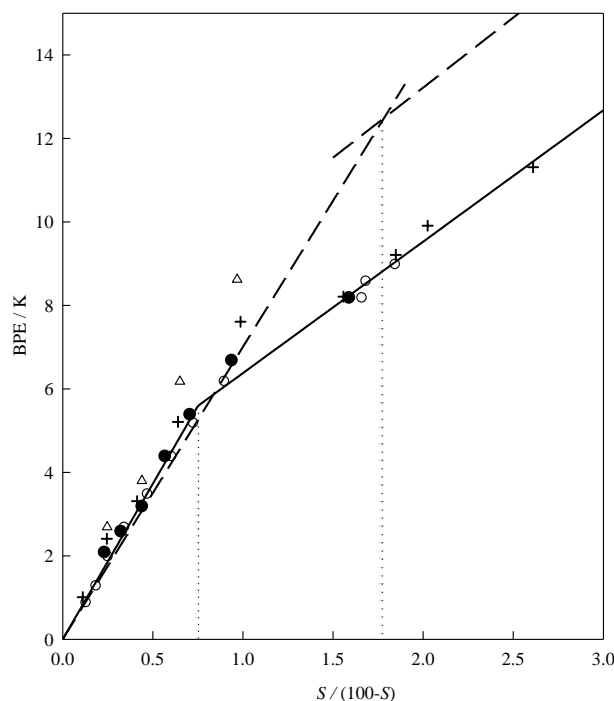


Figure 5 - Boiling point elevation, ΔT , as a function of the ratio of solids content to water, $S/(100-S)$ at atmospheric pressure: (●) BLSPA; (○) BLSPB; (+) BLSPC and (Δ) BLSPD. The solid lines represent the global behavior considering the liquors BLSPA, BLSPB and BLSPC. The long dashed lines represent the behavior of softwood black liquors (Slash pine)

Conclusions

In this paper, we present experimental data for the VLE and BPE of black liquors from a Kraft *Eucalyptus* mill. We give the mean value of the necessary heat for evaporation of the liquor and the variation of the BPE with the solids concentration. The representation of the BPE with the ratio of solids to water allows concluding that burkeite starts to precipitate at a value nearly to 45% of solids content: This value is lower than the one which is usually found to softwood species. More work must be done in the future to clarify some aspects raised by the

measurements presented here. For future work, it is planned (i) to improve the installation of VLE measurements; (ii) to study the effect of the pulping conditions, such as the cooking time, temperature and composition; (iii) to develop equations valid for the industrial conditions of the kraft chemical recovery process.

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