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The Surface Tension of Kraft Black Liquor from Eucalyptus

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Abstract. The surface tension of kraft black liquor from eucalyptus has been measured between 20 and 70ºC for solids content ranging up to 54 per cent. The dependence of the surface tension on the solids content follows the general pattern observed for black liquors from other woods. An empirical correlation describing the dependence of the surface tension on temperature and on solids content was established. This correlation can be applied to the actual conditions found in the chemicals recovery cycle of the kraft pulping process.
Key words: black liquor; eucalyptus; kraft; solids content; temperature

Medição da Tensão Superficial do Licor Negro do Eucalipto

Sumário. Mediu-se a tensão superficial do licor negro resultante do cozimento kraft industrial de aparas de eucalipto, com teor de sólidos até 54 por cento (em massa) na gama de temperaturas compreendida entre 20 e 70ºC. A variação da tensão superficial deste licor em função do teor de sólidos segue o comportamento padrão observado para licores provenientes de outras madeiras. Foi estabelecida uma correlação entre a tensão superficial do licor negro, a temperatura e o teor de sólidos, aplicável às condições que, na prática, são encontradas no ciclo de recuperação de químicos no processo kraft.
Palavras-chave: licor negro; eucalipto; kraft; teor de sólidos; temperatura

La Tension Superficielle des Liqueurs Noires d'Eucalyptus

Résumé. La tension superficielle des liqueurs noires d'eucalyptus (kraft) a été mesurée en fonction de la teneur en solides dissous, jusqu'aux 54 pour cent, et de la température comprise entre 20 et 70ºC. La dépendance de la tension superficielle suit une conduite générique observée pour les liqueurs noires d'autres bois. Une corrélation entre la tension superficielle, la température et la teneur en solides dissous a été établie. Cette corrélation peut être appliquée au procédé industriel de récupération des chimiques.
Mots clés: liqueur noire; eucalyptus; kraft; solides dissous; température

Introduction

Black liquor is the spent suspension that is collected from the brown stock washing after alkaline pulping. It contains organic dissolved wood residues and inorganic cooking components in a alkaline aqueous medium. The black

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liquor concentration is usually measured by drying liquid samples under specified conditions, and is expressed as the mass percentage of solids in the sample. At the outlet of the digestor black liquor generally contains 14 to 20 per cent of dissolved solids (weak black liquor). In the evaporation/concentration units the liquor is concentrated up to about 68 solids per cent (strong black liquor) using multiple effect evaporators. After concentration the black liquor is burnt in a recovery boiler which produces high pressure steam, to generate electricity, and low pressure steam, for process use. The properties of black liquor of interest in the evaporation process are the viscosity, the boiling point elevation, the density, the heat capacity, the surface tension, and the thermal conductivity. Viscosity and surface tension influence spray size distribution and black liquor droplet combustion, and thus the performance of the recovery boiler. Surface tension is important in black liquor drop formation during the spraying and nucleate boiling. It is also of importance in the characterization of surface active agents that can be present in the liquors (SODERHJELM and KOIVUNIEMI, 1982).

A large body of studies has been published on black liquor properties over the past two decades. However, not much information is available for surface tension. Studies of the influence of temperature and solids content on surface tension can be found in KRISHNAGOPALAN *et al.*, 1986, SODERHJELM and KOIVUNIEMI, 1982, and BECKWITH *et al.*, 1981. Recent published data from work with both softwood and hardwood indicates that, for a fixed temperature, the surface tension follows a general pattern: after falling rapidly with increasing solids content a minimum is observed between 10 and 40 per cent of solids content (SODERHJELM and KOIVUNIEMI, 1982). The composition of the organic part of black liquor influences strongly the measured surface tension: tall oil and turpentine are the most important agents in lowering the surface tension (BECKWITH *et al.*, 1981). However data on the effect of liquor composition on the surface tension are scarce. A particular factor which influences surface tension measurements (and mill operation) is the time needed to reach equilibrium conditions: at the beginning of the measurements the surface tension is high (near that for water) and after several seconds it falls to near the equilibrium value, following an assymptotical behaviour (SODERHJELM and KOIVUNIEMI, 1982). This critical factor influences the drop formation in the recovery boiler where the residence time is of the order of one second. For black liquor from eucalyptus pulp there is an almost complete lack of measured values reported in the literature. Since the Portuguese industrial pulpmaking processes use eucalyptus as the main raw material we have sistematically measured some properties of such kraft black liquors. Values of the viscosity have been reported for a wide range of temperature and solids content (GONÇALVES and LOBO, 1993). In this work we present the results of an experimental research work carried out in our laboratory in which we have measured and correlated the surface tension of black liquor resulting from the cooking of eucalyptus wood.

Experimental

Black liquor suspensions with different solids content were prepared from an original sample taken from the outlet of the evaporation and concentration plant of a Portucel mill. The composition parameters of the original sample as well as the methods of analysis used are reported in Table 1.

Table 1 – Composition parameters and methods of analysis for the black liquor sample

Parameter	Value	Method used
Alcalinity (as Na_2O)	21.4	NP421
Sulfidity (as Na_2O)	2.7	Tappi 625 om
Na+	21.2	FS
Solids content	67.6	Tappi 650 om

Several black liquor suspensions were prepared from the original sample, covering the range of solids content between 3.7 and 53.6 per cent. The mass of water m_{H2O} which must be added to the mass of original sample m_{or} to obtain a suspension of solids content S_f is obtained by mass balance to the solids:

$$m_{H_2O} = m_{or}\left(\frac{S_{or}}{S_f} - 1\right)$$

where S_{or} (= 67.6 mass per cent) is the solids content of the original sample. The true value of the solids content of each suspension was determined according to Tappi 650 om-69 standard. The surface tension of the suspensions was measured using a PC controlled KSV SIGMA 70 tension balance which employs the Du Nouy ring detachement and the Wilhelmy plate methods. The measurement probes -platinum/iridium ring, and plate - were thoroughly cleaned and flamed before each measurement. The measurements were automatically corrected to the actual values by means of the Hug and Mason compensation for interface distortion (HUG and MASON, 1975). To apply this correction the density of the black liquor suspension was calculated using experimental data taken from FRICKE, 1985. The temperature inside the surface tension measurement vessel was maintained and controlled to ±0.01 K using a Julabo FP50 thermostatic bath. The precision of the surface tension measurements is ±0.01 $mN.m^{-1}$. The performance of the tension balance was checked by measuring the surface tension of standard liquids: tridistilled water and n-heptane (LAB--Scan with a purity > 99%). The average percentual deviations APD, for M data points,

$$APD = 100\sum_{i=1}^{M}\frac{|(\sigma_{exp} - \sigma_{lit})|/\sigma_{lit}}{M} ,$$

where σ_{exp} and σ_{lit} represent the surface tension values obtained in this work and those from the literature, respectively, were 0.3 and 0.5 per cent for water and n-heptane, respectively, in the range 20 to 70ºC. The values of the surface tension measured in this work have been compared with those given in the literature for water (JASPER, 1972; VARGAFTIK, 1983) and for n-heptane (JASPER, 1972). The temperature probe of the tensiometer was calibrated against standard thermometers: (i) a precision mercury standard, graduate to 0.01ºC, certified by NPL (UK), for temperatures up to 42ºC; (ii) a certified Avantec digital thermometer (type p555 with a PT 100 probe) for temperatures higher than 42ºC. For each of the suspensions prepared from the original sample the surface tension has been measured starting at the lowest possible temperature according the solids content: for S =3.7 per cent this temperature was 20ºC; for the sample with 53.6 per cent of solids content the high consistency prevents measurements of the surface tension at temperatures below 30ºC. The maximum temperature achieved was near 70ºC for all the measurements. The Du Nouy ring probe method was used up to S= 20%; for higher solids content the large consistence of the black liquor forced the use of the Wilhelmy plate probe. In this situation a thin film is formed at the surface of the liquor making the measurements difficult to be made: the surface tension was high at the begining but reached practically a constant value after a few seconds.

Results and discussion

For each sample with a fixed value of solids content a number of measurements (about 100) of surface tension were made. The following procedure was then used to find the value of the surface tension at fixed values of the temperature: a number of measurements of the surface tension at neighbouring temperatures of the selected temperature were fitted to a linear function. The value of the surface tension at the fixed temperature considered was then calculated from the relation obtained. The results of this procedure are shown in Table 2.

Our data for the surface tension of water in the range 20 to 70ºC can be represented as a function of temperature by the equation

$$\gamma_w = 118.67 - 1.56 \times 10^{-1} T \,, \qquad (1)$$

with a standard deviation of ±0.07 mN.m^{-1}, a correlation coefficient r = =0.9973, and APD = 0.3% using for comparison the data from JASPER, 1972 and VARGAFTIK, 1983.

As expected the surface tension of each sample of black liquor decreases with increasing temperature, for a fixed value of solids content. The results in Table 2 are well represented by the following model:

$$\gamma = \gamma_w + s(1-s)\,\frac{a_1 + a_2 T}{1 + b_1(2s-1) + b_2(2s-1)^2} \,, \qquad (2)$$

where γ_w is the surface tension of pure water (S=0), given by equation (1), and s= S/100 is the weight fraction of solids. The parameters a_1, a_2, b_1 and b_2 obtained by fitting to data using the Levenberg-Marquardt method and are given in Table 3.

Table 2 – Dependence of eucalyptus black liquor surface tension σ (mN.m^{-1}) on temperature T (K), and solids content S(%)

$T/(K)$	γ / (mN.m^{-1})									
	S = 0 (ring)	**S=3.7% (ring)**	**S=3.7% (plate)**	**S=6.0% (ring)**	**S=11.9% (plate)**	**S=21.7% (ring)**	**S=21.7% (plate)**	**S=35.0% (plate)**	**S=45.7% (plate)**	**S=53.6% (plate)**
293.15	72.91	40.85	40.31	36.45	33.17	31.74	31.85	32.63	32.42	-
298.15	72.20	40.24	39.29	35.48	32.70	31.01	31.49	32.27	32.39	-
303.15	71.40	39.20	38.81	34.31	32.14	30.30	30.57	32.00	32.11	
308.15	70.77	38.63	38.12	33.14	30.64	29.50	29.57	31.57	31.75	41.20
313.15	69.75	37.93	37.10	32.32	30.56	28.60	28.87	31.27	31.29	39.50
318.15	68.82	37.23	37.25	31.20	29.28	27.86	27.95	30.97	31.10	35.25
323.15	68.30	35.64	35.44	30.30	28.79	27.69	27.79	30.80	30.70	31.59
328.15	67.81	35.55	34.98	29.60	27.72	26.20	26.15	30.30	30.40	29.37
333.15	67.05	34.96	33.94	28.59	26.90	24.49	25.24	29.78		
338.15	65.83	33.84	33.13	26.76	25.85	24.09	24.32	29.60		
343.15	64.94	33.22	32.42	26.35	24.69	23.39	23.44	29.08		

The experimental results and their representation using equation (2) are plotted in Figure 1, giving γ as a function of the solids content for selected values of the temperature. After a steep fall with the increase of solids content the surface tension reaches a value between 40 to 50 per cent that of pure water and goes through a flat minimum between 10 and 30 % of solids content. This behaviour was already pointed out for hardwood and softwood species (SODERHJELM and KOIVUNIEMI, 1982). In Figure 2 our data are compared with those for pine and for birch at 90ºC (SODERHJELM and KOIVUNIEMI, 1982). The minimum of the curve obtained in this work corresponds to (S = 20%, γ = 20 mN.m^{-1}), in close agreement to the observed minimum for pine wood. At higher values of solids content (S > 30%) the predicted surface tension from equation (2) is close to that observed for birch. A tridimensional plot showing the dependence of the surface tension on solids content S, and temperature T, resulting from equation (2), is shown in Figure 3.

Table 3 – Values of the parameters in equation (2)

a_1	a_2	b_1	b_2	$\sigma/(mN.m^{-1})$	r
-153.06	3.16x10^{-2}	4.09x10^{-1}	-5.43x10^{-1}	± 1.47	0.994

σ is the standard deviation of γ, and r is the correlation coefficient

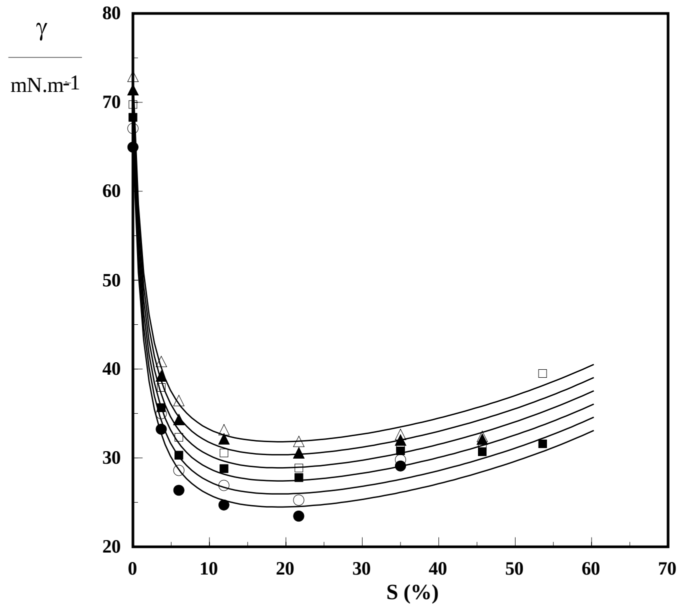

Figure 1 – Surface tension of eucalyptus black liquor as a function of solids content (in mass percent) and of the temperature (in K). The curves are obtained from equation (2), and the symbols represent the experimental data. Legend: □,T=293.15K; ▲, T=303.15K;□, T=313.15K; ■, T=323.15K; ○, T= 333:15K; ●, T=343.15K

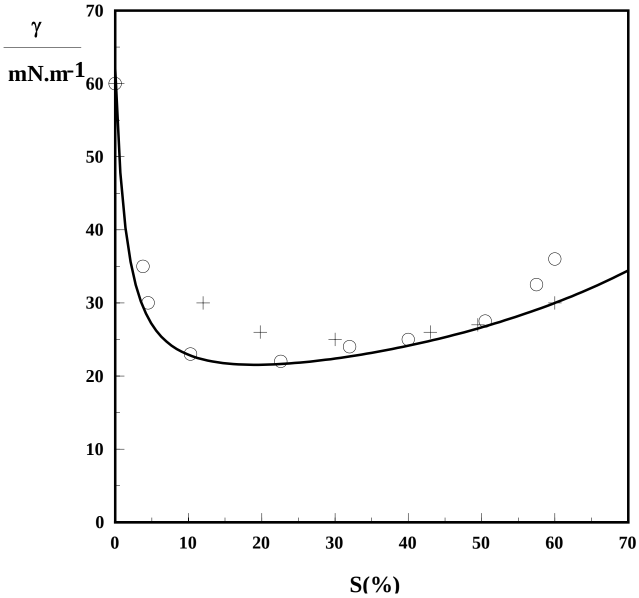

Figure 2 – Surface tension of black liquor as a function of solids content S, at 90ºC. The solid curve is obtained from equation (2). The symbols correspond to the experimental data from SODERHJELM, L., KOIVUNIEMI, U.: (○) pine; (+) birch

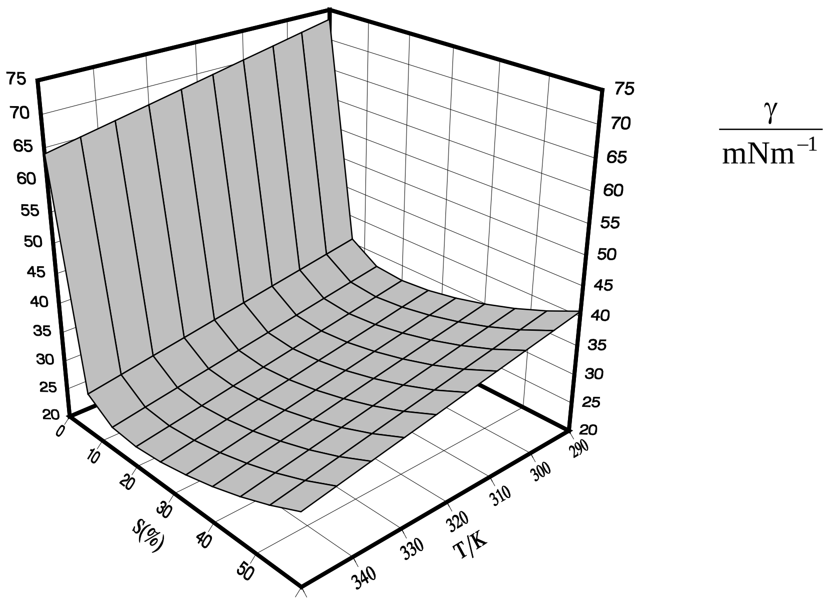

Figure 3 – Surface tension of black liquor as a function of solids content and temperature. Surface calculated from equation (2)

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