# Effect of Extended Cooking and Oxygen Prebleaching on the Surface Energy of Eucalyptus globulus Kraft Pulps

M.G. CARVALHO, P.J. FERREIRA, J.M.R.C.A. SANTOS, J.L. AMARAL and M.M. FIGUEIREDO

The aim of this work was to investigate the influence of introducing an oxygen prebleaching stage and of extending the cooking process on the surface and papermaking properties of elemental chlorine-free bleached kraft pulps produced with Portuguese Eucalyptus globulus. Inverse gas chromatography was used to evaluate the surface energy as well as the Lewis acid/base character of the pulps, taking as reference one pulp cooked and bleached under standard conditions. The dispersive component of the surface tension,  $\gamma_s^d$ , was found to be highest for the pulp prepared under standard conditions, lowest for the pulp prepared by extended cooking and intermediate for the oxygen-prebleached pulp. Although all pulps exhibited a dominant acidic character ( $K_a/K_b > 1$ ), the oxygen stage was found to enhance this character due to the higher surface concentration of oxygen-containing functional groups. Furthermore, oxygen prebleaching led to the formation of bulkier handsheets and it increased the beating energy. The opposite behaviour was found for the pulp produced by increasing the H-factor to extend the cooking.

Dans le présent travail, nous avions à analyser l'influence de l'introduction d'une étape de pré blanchiment à l'oxygène et du prolongement de la cuisson sur les propriétés de surface et de fabrication des pâtes kraft blanchies sans chlore élémentaire produites à partir d'Eucalyptus globulus portugais. Nous avons utilisé la chromatographie inversée en phase gazeuse pour évaluer la tension superficielle ainsi que les caractéristiques acidebase de Lewis des pâtes, en prenant comme référence une pâte cuite et blanchie dans des conditions standard. Nous avons trouvé que la composante dispersive de la tension superficielle,  $\gamma_s^4$ , était la plus élevée pour la pâte préparée dans des conditions standard, la plus faible pour la pâte préparée par une cuisson prolongée, et intermédiaire pour la pâte préblanchie à l'oxygène. Bien que toutes les pâtes aient présenté un caractère acide dominant  $(K_a/K_b>1)$ , nous avons trouvé que l'étape de l'oxygène accroissait cette caractéristique en raison de la plus grande concentration à la surface des groupes fonctionnels contenant de l'oxygène. De plus, le pré blanchiment à l'oxygène a produit des formettes plus bouffantes et exigé davantage d'énergie de raffinage en pile. Nous avons aussi obtenu un comportement opposé de la pâte produite en accroissant le facteur H pour prolonger la cuisson.

## INTRODUCTION

Ink-jet printing has been considered one

JPPS

M.G. Carvalho, P.J. Ferreira and M.M. Figueiredo Univ. Coimbra Dept. Chem. Engin. Pólo II, Pinhal de Marrocos 3030-290 Coimbra, Portugal (mgc@eq.uc.pt) J.M.R.C.A. Santos Polytechnic Inst. Bragança Dept. Chemical Technol. Campus de Santa Apolónia 5301-857 Bragança, Portugal J.L. Amaral RAIZ - Forest Paper Res. Inst. Quinta de S. Francisco Apartado 15 3801-501 Eixo, Portugal

of the leading printing processes and, accordingly, has been the subject of many research studies. Terms such as printability, which describes the paper surface characteristics that influence the quality of the printed surface in relation to ink and press combinations, are now in current use by papermakers [1]. To understand the printing process, it is necessary to examine the surface properties of paper, especially its surface free energy [2,3], which affects the adhesive properties and also the spreading of a liquid over the surface and its penetration into the fibre network.

It is well known that the surface energy of the paper sheet, as well as the chemical characteristics of the paper surface and of the ink, is important in printing. However, other physical properties, such as the nature of fibres and the structure of the fibre network, must also be

taken into consideration to establish correlations with the interfacial phenomena that affect the interactions between paper and ink.

Portuguese Eucalyptus globulus fibres are generally considered of good quality for the production of printing papers, particularly for those intended to be used with ink-jet printers. Although the fibrous component is a major determinant of the paper surface properties and their interaction with binders, additives and inks, differences in cooking, bleaching and papermaking will also affect the ink-jet printing quality of the paper, since they influence the surface chemical composition and, consequently, the surface free energy. A number of studies have been carried out to investigate and modify the surface properties of fibres aiming at the identification of the major factors that affect the aforementioned interfacial phenomena [4]. Properties such as surface free energy and Lewis acid/base character have been used as crucial tools to investigate the surface composition of cellulosic fibres and to understand the way in which different pulping processes as well as different treatments will affect the pulp surface chemical composition [5–9].

Due to environmental concerns, attempts have been made worldwide to reduce the amount of adsorbable organic halogen (AOX) compounds and the chemical oxygen demand load in an elemental chlorine-free (ECF) bleach plant by decreasing the kappa number prior to bleaching. One way to achieve this is to extend the cooking process. In fact, several modified kraft processes have been developed to reach that objective without losing pulp yield, but the pulp quality is always negatively affected. Alternatively, delignification has been introduced by many pulp mills into the conventional ECF bleaching process (for instance, using ODEDED instead of the DEDED sequence), although the introduction of this stage also causes a deterioration in pulp quality. The main objective of the present work was to study the influence of these two strategies on the surface energetics of Eucalyptus globulus bleached pulps and on corresponding papermaking properties. The properties that most affect the printability have been studied thoroughly already, but little work has been done concerning their relationship to the surface characteristics of fibres and paper.

#### METHODOLOGY Pulps Production

Portuguese Eucalyptus globulus chips were used to produce three different samples of bleached kraft pulp. As indicated in Table I, two of them (EG-1 and EG-2) were obtained by using the same cooking conditions in an MK laboratory digester (model 409 MII from M/K Systems, Inc., Danvers, MA, USA, with a capacity of ~7 L) whereas, for the third case (pulp EG-3), a higher H-factor was used (by increasing cooking temperature and time), resulting in an unbleached pulp with a lower kappa number. To study the influence of a predelignification stage with oxygen, pulps EG-1 and EG-2 were bleached by applying DEDED and ODEDED sequences, respectively. Pulp EG-3 also was bleached by the conventional ECF sequence (DEDED). A value of 90% ISO final brightness was achieved for the three pulps. Due to the standard cooking and bleaching conditions, pulp EG-1 was considered the reference pulp. For inverse gas chromatography (IGC) measurements, all the bleached pulps were dried at room temperature, oven dried at 105°C for 2 h and milled.

Measurements of physical properties were performed on handsheets of unbeaten and beaten pulps. The latter were obtained in a PFI laboratory mill to achieve a Schopper-Riegler freeness of 30 (ISO 5263 [10], ISO 5264/2 [11], ISO 5267/1 [12]). For both the unbeaten and the beaten pulps, fibre length and fines content were measured using the Fiber Quality Analyzer (FQA), OpTest Inc., Hawkesbury, ON, Canada. Handsheets were prepared and tested

TABLE I
PROCESS CONDITIONS FOR THE VARIOUS E. globulus PULPS (ACTIVE ALKALI
CHARGE 16% Na<sub>2</sub>O, SULPHIDITY 30%, LIQUOR TO WOOD RATIO 4, HEATING RATE 1°/min)

	<b>E</b> G-1	EG-2	EG-3
Temperature, °C	160	160	165
Time at temperature, min	45	45	50
Kappa number	14.8	14.8	12.5
Bleaching sequence (90% ISO brightness)	DEDED	ODEDED	DEDED

TABLE II
CHARACTERISTICS OF IGC PROBES [2,24]

	A nm²	γ <sup>d</sup> mJ/m²	<i>AN*</i> kJ/mol	<i>DN</i> kJ/mol
Alkanes				
C <sub>6</sub> H <sub>14</sub>	0.514	18.4		
C <sub>7</sub> H <sub>16</sub>	0.570	20.3		원생생 그리
C <sub>8</sub> H <sub>18</sub>	0.628	21.3	<b></b>	
C <sub>9</sub> H <sub>20</sub>	0.689	22.7		_
C <sub>10</sub> H <sub>22</sub>	0.750	23.9		
Polar probes	그 기가 나타를 받다			
Chloroform	0.440	25.0	22.7	n
Tetrahydrofuran	0.450	22.5	2.1	84.1
Acetone	0.425	16.5	10.5	71.2

A = cross-sectional area,  $\gamma_I^d$  = dispersive component of the surface tension, AN\* = Gutmann's modified acceptor number and DN = Gutmann's donor number.

against the most common structural, optical and mechanical standards (bulk, Gurley air resistance, Bendtsen roughness, light scattering coefficient, tensile and tear strength – ISO 5269/1 [13], ISO 534 [14], ISO 536 [15], ISO 5636/5 [16], ISO 87912 [17], ISO 9416 [18], ISO 1924/2 [19], ISO 1974 [20]).

# **IGC** Technique

IGC has been reported as a powerful tool to study surface energetics and Lewis acid/base character for a large number of materials [2–5,21]. According to the Fowkes theory [22], the surface free energy can be considered as the sum of components of various origins, the most relevant being the dispersive component arising from London and Van der Waals forces, and the specific component due to Lewis acid/base interactions and hydrogen bonding. To evaluate the surface interaction capability of cellulosic fibres, IGC was used to determine the dispersive component of their surface tension  $(\gamma_s^a)$  and to analyze their Lewis acid/base character.

IGC is similar to conventional gas chromatography, the main difference being the fact that the material under study is the stationary phase inside the chromatographic column and the compounds injected (probes) have wellknown properties. A Perkin Elmer (Boston, MA, USA) 8410 gas chromatograph equipped with a hydrogen flame ionization detector was used for IGC data collection. This instrument was connected to a Kompensograph Siemens (Berlin, Germany) integrator. Stainless steel columns 0.5 m long and 0.4 mm ID, degreased, washed and dried, were packed with the ovendried milled pulp using a vacuum pump. The packed columns were conditioned at 105°C overnight under a helium flow before any measurements were taken,

Measurements were carried out at col-

umn temperatures that ranged from 40 to 60°C, at 5°C intervals. The injector and detector were kept at 180 and 200°C, respectively. The carrier gas (helium) flow in each column was optimized to ensure that neither absorption nor diffusion of the probes would occur in the column stationary phase. This was achieved by determining the retention volume of octane at several helium flow rates for the temperature range in which the experiments were undertaken.

Minute quantities of probe vapour (<1 μL) were injected into the carrier gas flow to ensure that the experiments take place at infinite dilution. Chromatographic grade (Sigma-Aldrich Ltd., St. Louis, MO, USA) probes were used without further purification. Their relevant properties are listed in Table II. Natural gas with 83.7% methane was used to determine the dead retention volume. Replicate measurements were performed using two columns prepared in the same way. Retention times were the average of at least five injections. The peaks obtained using the modified gas chromatograph unit were reproducible and the retention times were independent of the probe quantity injected. Reproducibility between runs was always better than 2%. The retention times were determined graphically according to the Conder and Young method [23].

# **IGC Data Analysis**

The theory relating thermodynamic functions to IGC experimental data is discussed thoroughly and reported in the literature [2–5,21] and will be mentioned only briefly here. For each probe tested, the retention time,  $t_n$ , is used to calculate the net retention volume, Vn, as:

$$Vn = (t_r - t_0)F \cdot J \tag{1}$$

where  $t_0$  is the dead retention time of the marker probe (methane), F is the carrier gas flow rate (measured with a digital flow meter) and J is the correction factor for gas compressibility which is related to the inlet pressure, Pi, and the outlet pressure, Po, by:

$$J = \frac{3}{2} \left[ \frac{(Pi/Po)^2 - 1}{(Pi/Po)^3 - 1} \right]$$
 (2)

Assuming that the experiments take place at infinite dilution, the free energy of adsorption of the probe on the stationary phase surface per mole,  $\Delta G$ , can be determined from the retention volume, Vn, according to:

$$\Delta G = -RT \ln(Vn) + C_1 \tag{3}$$

where R is the gas constant, T is the absolute column temperature and  $C_1$  is a constant which depends on the chromatographic column and on the reference state. Considering, as suggested by Fowkes [22], that the dispersive and specific components,  $\Delta G^d$  and  $\Delta G^s$ , respectively, are additive, Eq. (3) can be rewritten as:

$$\Delta G^d + \Delta G^s = -RT \ln(Vn) + C_1 \tag{4}$$

On the other hand, the free energy of adsorption can be related to the work of adhesion, *Wa* [25], according to:

$$-\Delta G = N \cdot A \cdot Wa + C_2 \tag{5}$$

where N is Avogadro's number, A is the crosssectional area of the probe to be tested (Table II) and  $C_2$  is a constant. If nonpolar components (such as n-alkanes) are used, only dispersive interactions occur and the work of adhesion is given by:

$$Wa = 2\left(\gamma_s^d \gamma_l^d\right)^{1/2} \tag{6}$$

where  $\gamma_s^d$  and  $\gamma_I^d$  are the dispersive components of surface free energy of the solid (stationary phase) and of the liquid surfaces, respectively. Substituting Eqs. (5) and (6) in Eq. (3) leads to:

$$2N\left(\gamma_s^d\right)^{1/2}A\left(\gamma_l^d\right)^{1/2} + C = RT\ln(Vn) \tag{7}$$

The slope of the straight line obtained by plotting  $RT\ln(Vn)$  versus  $2N(\gamma_l^d)^{1/2}A$ , for a homologous n-alkane series, leads to the determination of  $\gamma_s^d$  for a given temperature.

The Lewis acid/base characteristics of a fibre surface are determined by analyzing the interaction of the polar probes with the solid surface and by quantifying the deviation from the reference line (obtained with the n-alkane probe series), leading to the estimation of the specific free energy,  $\Delta G^s$ , as:

$$-\Delta G^{s} = RT \ln(Vn) - RT \ln(Vn_{ref})$$
 (8)

where  $Vn_{ref}$  is the retention volume obtained using the n-alkane reference line (Eq. 1) and Vn is the retention volume of the polar probes. The work of adhesion between the probes tested and the fibres can be evaluated from the free energy, by combining Eqs. (5) and (8):

TABLE III
VISCOSITY AND CHLORINE DIOXIDE CONSUMPTION FOR THE PULPS

		EG-1 EG-3
Viscosity, dm³/kg		1478 1478 1335 4.30 2.37 3.45
ClO <sub>2</sub> charge, % as Cl <sub>2</sub> Viscosity after bleaching, dm	³/kg	4.30 2.37 3.45 1245 1127 1193

# TABLE IV IGC RESULTS FOR PULPS EG-1, EG-2 AND EG-3

$\gamma_S^d$ $(40^{\circ}\text{C})$ $ ext{d}\gamma_S^d/ ext{d} au$ $ ext{Wa}(\text{THF})/Wa(\text{CF})$ $(mJ/\text{m}^2\text{T})$ $(at 40^{\circ}\text{C})$	ICI₃) <i>K∤K₅</i>
EG-1 41.3 -0.25 2.3 EG-2 35.1 -0.62 3.7 EG-3 12.6 -0.35 1.5	2.8 6.1 2.6

 $\gamma_s^d$  = dispersive component of surface tension,  $Wa(THF)/Wa(CHCl_3)$  = work of adhesion ratio and  $K_d/K_b$  = Lewis acid/base character.

$$Wa = \frac{RT}{N \cdot A} \ln \left( \frac{Vn}{Vn_{ref}} \right) \tag{9}$$

If the experiments take place at different temperatures, it is possible to determine the enthalpy of adsorption,  $\Delta H^s$  and the entropy of adsorption,  $\Delta S^s$ , by plotting  $\Delta G^s/T$  versus 1/T according to the following equation:

$$\frac{\Delta G^s}{T} = \frac{\Delta H^s}{T} - \Delta S^s \tag{10}$$

The acidic and basic constants,  $K_a$  and  $K_b$ , respectively, are calculated using Eq. (11) from the plot of  $\Delta H^s/AN^*$  versus  $DN/AN^*$ .  $AN^*$  and DN are, respectively, the modified acceptor and donor numbers of the probes tested (Table II).

$$\frac{\left(-\Delta H^{s}\right)}{AN^{*}} = K_{a} \frac{DN}{AN^{*}} + K_{b} \tag{11}$$

# RESULTS AND DISCUSSION

As expected, extended cooking leads to a reduction not only of the kappa number but also of the pulp viscosity (Table III). In addition, this strategy diminishes (~20%) the chlorine dioxide charge needed to reach the same brightness, but the bleached pulp exhibits a lower viscosity (~52 units) compared to the reference pulp. On the other hand, oxygen delignification allows a greater reduction in ClO<sub>2</sub> charge (~45%) but, nevertheless, leads to the highest decrease in pulp viscosity (~120 units). Usually, these O pulps correspond to lower physical-mechanical quality, since viscosity has been related to polysaccharide degradation [26]. In fact, as will be shown later, the oxygen stage reduces pulp fibre length, beatability and tensile strength. In some cases, these features may be considered as a real handicap for incorporating an oxygen stage into the ECF bleaching sequence in spite of the positive influence of this procedure on the reduction of the AOX level in the mill effluent.

## **IGC Results**

Table IV summarizes the IGC results ob-

tained for the pulps tested with respect to the dispersive component of surface tension  $(\gamma_s^d)$ , its variation with temperature  $(\mathrm{d}\gamma_s^d/\mathrm{d}T)$ , as well as the Lewis acid/base character, given by the ratio between the work of adhesion for the model basic probe and the model acidic probe (tetrahydrofuran (THF) and chloroform, respectively). In addition, the Lewis acidic and basic constants  $(K_a$  and  $K_b)$  of the fibre surface were calculated, their ratio being also listed in Table IV.

With regard to the dispersive component of the surface tension, it was found that the value obtained for pulp EG-1 is comparable to that reported in the literature for a fully bleached kraft pulp produced with Australian eucalypt ( $\gamma_s^d = 38.4 \text{ mJ/m}^2 \text{ at } 40^{\circ}\text{C}$ ) [6]. The oxygen predelignified pulp (EG-2) exhibited a slightly lower value that could be due to the higher content of residual lignin and extractives (both with lower surface energy than that of cellulose) found in nonconventional bleached pulps, which tend to accumulate on the fibre surface [7,27]. Besides, as will be seen later, this pulp also possesses a higher content of fines, which most certainly contributes to enhance these effects [6]. The value found for  $\gamma_s^d$ in pulp EG-3, at 40°C, is significantly lower than those for pulps EG-1 and EG-2. Extrapolation of the  $\gamma_s^d$  value for sample EG-3 to room temperature (22°C) yields the value of 19 mJ/m2. Although unusual for eucalypt pulps, these low  $\gamma_s^d$  values are in agreement with those reported in the literature for kraft and explosion pulps [28]. Moreover, the value of  $\gamma_s^d$  relates to the dispersive component of the surface tension only and, thus, the total surface tension value is expected to be somewhat greater due to the contribution of the Lewis acid/base intermolecular forces to the surface free energy. The value of the ratio  $K_a/K_b$  for this sample is in the same order of magnitude as that of sample EG-1. This fact, along with the good correlation coefficients obtained from the linear regressions performed in the experimental data, indicates that the IGC technique and data reduction procedures are valid. One possible cause for this

decrease in  $\gamma_s^d$  is the fact that, due to the high cooking temperature, the residual lignin or extractives could react further, leading to the formation of more condensed structures. The concentration of these structures at the fibre surface renders more difficult their removal by the bleaching chemicals and, thus, tends to reduce the surface energy. Finally, it should be mentioned that additional measurements conducted on samples EG-1 and EG-3 extracted with dichloromethane resulted in a very significant increase of  $\gamma_s^d$  for the EG-3 fibres (38.6) mJ/m<sup>2</sup> after extraction) whereas, for EG-1, only a slight increase was observed (43.3 mJ/m<sup>2</sup>). The work of adhesion and  $K_a/K_h$  ratios were not changed significantly. This evidence further supports the interpretation that the low value of  $\gamma_s^d$  for the EG-3 fibres is due to the presence of extractives and residual lignin at

Figure 1 illustrates the linear decrease of  $\gamma_s^d$  with temperature for the various pulps studied, quantified in Table IV  $(\mathrm{d}\gamma_s^d/\mathrm{d}T)$ . The negative slope reflects an entropic contribution to the surface free energy and is in agreement with results published for other eucalypt kraft pulps [6,7]. These slopes are smaller (and closer to each other) for pulps EG-1 and EG-3 than for pulp EG-2, suggesting that the surface of the fibres of the latter pulp has a higher degree of freedom and is more sensitive to an entropic contribution of the surface free energy [7].

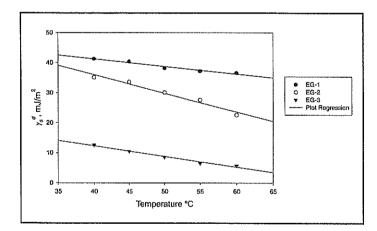
Regarding the Lewis acid/base characteristics of the fibre surface, all pulps showed a

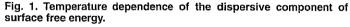
dominant acidic behaviour. As a matter of fact, both Wa(THF)/Wa(CHCl3) ratios listed in Table IV as well as the work of adhesion presented in Fig. 2 indicate a stronger interaction with the model basic probe (THF), especially that of pulp EG-2. This is most certainly due to the incorporation of an oxygen stage in the bleaching process, which causes a stronger oxidation of the surface, increasing the amount of oxygen-containing functional groups such as the carboxylic group [27]. Besides, Fig. 2 also shows that the work of adhesion with the model basic probe (THF) is much higher for the oxygen-bleached pulp (about twice) than for the other pulps, whereas the work of adhesion between the model acidic probe (CHCl3) and the fibres gradually increases from pulp EG-1 to pulp EG-3. Consequently, the latter pulp exhibits the lowest Wa(THF)/Wa(CHCl3) ratio. As mentioned before, the acid/base character was assessed alternatively by the values of the  $K_a/K_b$  ratios, also presented in Table IV. However, it should be pointed out that the work of adhesion, determined from the free energy of adsorption, includes the entropic effect involved in the acid-base interaction, whereas the calculation of acidic and basic constants is based on the adsorption enthalpy. The two methods are generally in good agreement with respect to relative variations, but the absolute values may not be directly correlated [8]. Indeed, as can be seen from Table IV, the  $K_a/K_b$ ratios reveal the same tendency as those obtained for the work of adhesion, confirming that

all pulps exhibited a chiefly acidic character, the highest value corresponding to pulp EG-2.

### Physical Properties

Table V summarizes some of the most important physical properties of the pulps studied and reveals that, before beating, pulp EG-2 is quite different from pulps EG-1 and EG-3. In fact, the amount of fines of pulp EG-2 is higher than that of the other two pulps and, accordingly, the average fibre length is shorter. This is probably the result of the oxygen predelignification stage which increases the detachment of some additional fibre wall material of very small dimensions. Furthermore, the unbeaten pulp EG-2 is also the one in which fibre bonding is less effective, as can be concluded from the properties of the corresponding handsheets: higher values for bulk, light-scattering coefficient and surface roughness and smaller values for air resistance and tensile index. This behaviour is related to the very strong Lewis acid character observed for this pulp, which disturbs the development of hydrogen bonds. However, in spite of producing bulkier handsheets, the drainability of this pulp is close to that of the other unbeaten pulps, most likely as a consequence of the greater amount of fines and of the important role of these in water retention. In addition, the stronger oxidation of pulp EG-2 affects its beatability, as can be seen from the higher amount of beating energy needed to achieve 30 SR (2000 rpm, compared to 1750 and 1500 rpm for pulps EG-1 and EG-3,





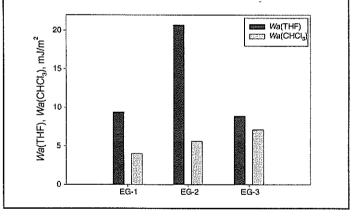


Fig. 2. Work of adhesion of fibres with model basic (THF) and model acidic (chloroform) probes at 400°C.

	EG-1		EG-2		EG-3	
	Unbeaten	Beaten	Unbeaten	Beaten	Unbeaten	Beaten
Revolutions, rpm	0	1750	0	2000	0	1500
Drainage, SR	19	30	18	30	19	30
Average fibre length, µm (length weighted)	765		720		760	
Fines content (n/n, %)	7.4		8.0		7.0	
Bulk, cm³/g	1.48	1.26	1.60	1.29	1.35	1.27
Air resistance (Gurley), s/100 mL	2.7	20.8	1.2	22.2	3.0	19.2
Bendtsen roughness, mL/min	182	88	330	92	155	98
Light-scattering coefficient, m <sup>2</sup> /kg	32.9	24.9	35.3	24.8	31.4	25.4
Tensile index, Nm/g	49	91	37	85	54	90
Tear index, mNm <sup>2</sup> /g	4.5	5.7	4.4	5.7	3.9	6.3

respectively). Nevertheless, as expected, the ODEDED pulp is the one which has better incorporated the changes promoted by the beating action, suggesting that, by external and internal fibrillation, more functional groups become available, resulting in an increment of fibre bonding.

The unbeaten pulp EG-3, obtained by using a higher *H*-factor, produces denser handsheets with increased bonded area and reduced air–fibre interfaces. This is explained by the more evenly bipolar surface of the fibres of this pulp (Fig. 2) that facilitates fibre bonding. Moreover, the degradation of the fibre wall structure during cooking, which improves the flexibility and collapsibility of these fibres, enhances their conformability. Accordingly, the extension of the beating action required by this pulp to reach the same Schopper-Riegler number as the other two pulps is smaller and the handsheet properties of the beaten pulp are similar to those of pulp EG-1.

## CONCLUSIONS

The present work has shown that the surface of eucalypt kraft fibres has a strong Lewis acid character and that the introduction of an oxygen stage prior to the ECF bleaching process greatly increases this character. On the contrary, the dispersive component of the surface tension after delignification with oxygen slightly decreases as a result of the deposition/migration to the fibre surface of some residual low-energy compounds, such as lignin and extractives. Besides, this pulp appears to be more sensitive to an entropic contribution to the surface free energy than conventionally bleached pulp fibres.

The stronger surface acidic character of the oxygen-delignified pulp fibres contributes to the formation of bulkier handsheets with higher surface roughness, air permeability and light scattering, as well as lower tensile resistance. This pulp also possesses the highest percentage of fines and, accordingly, the shortest average fibre length. On the other hand, although requiring more energy than the other pulps (bleached by the conventional bleaching sequence, DEDED) to reach 30 SR, the corresponding handsheet properties change more significantly with beating.

A moderately higher cooking temperature and time, although reducing the interactions of a dispersive nature, promote fibre bonding, either because of the more evenly bipolar surface of the fibres or the increase in fibre flexibility and collapsibility. The unbeaten fibres so produced give a more compact fibre network. Moreover, in these circumstances, beating energy decreases but the changes in paper properties induced by beating are more moderate than for the reference pulp.

## **ACKNOWLEDGEMENTS**

Thanks are due to Sapiens Program for the research grant (PE044-PE/PPQ/34159/99). The skillful work of A. Aquino (grant holder, Dept. Chem. Engin., University of Coimbra) in IGC analysis is also acknowledged.

## REFERENCES

- BANERJEE, R.K., "Surface Characterization of Paper and Printability", Proc. Indian Pulp Paper Tech. Assoc. Ann. Gen. Mtg., Developments in Pulp Mill and Paper Machine Clothings, New Delhi, India, 75–90 (1991).
- SANTOS, J.M.R.C.A, GIL, M.H., PORTUGAL, A. and GUTHRIE, J.T., "Characterization of the Surface of a Cellulosic Multi-Purpose Office Paper by Inverse Gas Chromatography", Cellulose 8:217-224 (2001).
- SANTOS, J.M.R.C.A., FAGELMAN, K. and GUTHRIE, J.T., "Characterisation of the Surface Lewis Acid/Base Properties of Poly(butylene terephthalate) by Inverse Gas Chromatography", J. Chromatography A 969(1-2):111-118 (2002).
- BELGACEM, M.N., "Characterization of Polysaccharides, Lignin and Other Woody Components by Inverse Gas Chromatography: A Review", Cellulose Chem. Technol. 34:357–383 (2000).
- BELGACEM, M.N., CZEREMUSZKIN, G. and SAPIEHA S., "Surface Characterization of Cellulose Fibres by XPS and Inverse Gas Chromatography", Cellulose 2:145–157 (1995).
- SHEN, W., YAO, W., LI, M. and PARKER, I., "Characterization of Eucalypt Fibre Surface Using Inverse Gas Chromatography and X-Ray Photoelectron Spectroscopy", Appita J. 51(2):47-51 (1998).
- SHEN, W., PARKER, I.H., and SHENG, Y.J., "The Effects of Surface Extractives and Lignin on the Surface Energy of Eucalypt Kraft Pulp Fibres", J. Adhesion Sci. Technol. 12(2):161-174 (1998).
- SHEN, W. and PARKER, I.H., "Surface Composition and Surface Energetics of Various Fural vnt Pulps". Cellulose 6:41-55 (1999).
- Eucalypt Pulps", Cellulose 6:41–55 (1999).
   LIU, F.P. and RIALS, T.G., "Relationship of Wood Surface Energy to Surface Composition", Langmuir 14:536–541 (1998).
- "Pulps Laboratory Wet Disintegration", ISO 5263, Intl. Org. Standardiz., Geneva, Switzerland (1995).
- "Pulps Laboratory Beating Part 2: PFI Mill Method", ISO 5264-2, Intl. Org. Standardiz., Geneva, Switzerland (2002).
- "Pulps Determination of Drainability Part 1: Schopper-Riegler Method", ISO 5267-1, Intl. Org. Standardiz., Geneva, Switzerland (1999).
- "Pulps Preparation of Laboratory Sheets for Physical Testing - Part 1: Conventional Sheet-Former Method", ISO 5269-1, Intl. Org. Standardiz., Geneva, Switzerland (1998).
- "Paper and Board Determination of Thickness and Apparent Bulk Density or Apparent Sheet Density", ISO 534, Intl. Org. Standardiz.,

- Geneva, Switzerland (1988).
- "Paper and Board Determination of Grammage", ISO 536, Intl. Org. Standardiz., Geneva, Switzerland (1995).
- "Paper and Board Determination of Air Permeance and Air Resistance (Medium Range) – Part 5: Gurley Method", ISO 5636-5, Intl. Org. Standardiz., Geneva, Switzerland (2003).
- "Paper and Board Determination of Roughness/Smoothness (Air Leak Methods) Part 2: Bendtsen Method", ISO 8791-2, Intl. Org. Standardiz., Geneva, Switzerland (1990).
- "Paper Determination of Light Scattering and Absorption Coefficients (Using Kubelka-Munk Theory)", ISO 9416, Intl. Org. Standardiz., Geneva, Switzerland (1998).
- "Paper and Board Determination of Tensile Properties – Part 2: Constant Rate of Elongation Method", ISO 1924-2, Intl. Org. Standardiz., Geneva, Switzerland (1994).
- "Paper Determination of Tearing Resistance (Elmendorf Method)", ISO 1974, Intl. Org. Standardiz., Geneva, Switzerland (1990).
- Standardiz., Geneva, Switzerland (1990).

  21. SANTOS, J.M.R.C.A., FAGELMAN, K. and GUTHRIE, J.T., "Characterisation of the Surface Lewis Acid/Base Properties of the Components of Pigmented, Impact-Modified, PC/PBT Blends by Inverse Gas Chromatography Phase Separation and Phase Preference", J. Chromatography A 969(1-2):119-132 (2002).
- FOWKES, F.M., "Role of Acid-Base Interfacial Bonding in Adhesion", J. Adhesion Sci. Technol. 1(1):7 (1987).
- KAMDEM, D.P. and RIEDL, B., "Inverse Gas Chromatography of Lignicellulosic Fibres Coated with a Thermosetting Polymer: Use of Peak Maximum and Conder and Young Methods", J. Colloid Interface Sci. 150:507-516 (1992).
- KAMDEM, D.P., BOSE, S.K. and LUNER, P., "Inverse Gas Chromatography Characterization of Birch Wood Meal", Langmuir 9(11):3039-3044 (1993).
- DORRIS, G.M. and GRAY, D.G., "Adsorption of n-Alkanes at Zero Surface Coverage on Cellulose Paper and Wood Fibres", J. Colloid Interface Sci. 77(35):353-362 (1980).
- CARVALHO, M.G., FERREIRA, P.J. and FIGUEIREDO, M.M., "Cellulose Depolymerisation and Paper Properties in E. globulus Kraft Pulps", Cellulose 7:359–368 (2000).
- LUNDQVIST, A., ODBERG, L. and BERG, J.C., "Surface Characterization of Non-Chlorine-Bleached Pulp Fibres and Calcium Carbonate Coatings Using Inverse Gas Chromatography", Tappi J. 78(5):139-142 (1995).
- CHTOUROU, H., RIEDL, B. and KOKTA, B.V., "Surface Characterization of Modified Polyethylene Pulp and Wood Pulp Fibres Using XPS and Inverse Gas Chromatography", J. Adhesion Sci. Technol. 9(5):551–574 (1995).

REFERENCE: CARVALHO, M.G., FERREIRA, P.J., SANTOS, J.M.R.C.A., AMARAL, J.L. and FIGUEIREDO, M.M., Effect of Extended Cooking and Oxygen Prebleaching on the Surface Energy of Eucalyptus globulus Kraft Pulps, Journal of Pulp and Paper Science, 31(2):90–94 April/May/June 2005. Paper offered as a contribution to the Journal of Pulp and Paper Science. Not to be reproduced without permission from the Pulp and Paper Technical Association of Canada. Manuscript received May 5, 2004; revised manuscript approved for publication by the Review Panel March 31, 2005.

KEYWORDS: EUCALYPTUS GLOBULUS, KRAFT PULPS, PRETREATMENT, OXYGEN, BLEACHED PULPS, PULP PROPERTIES, DISPERSION, SURFACE TENSION, OXYGEN PREBLEACHING.