The effect of surfactants on kraft pulping of *Pinus pinaster*

CECÍLIA BAPTISTA*, NACEUR BELGACEM† AND ANA PAULA DUARTE‡

SUMMARY

In order to ascertain the influence of surfactants in the delignification of *Pinus pinaster* wood and the bleachability of the resulting pulps, 17 surfactants from four families of surfactants were tested, namely: cationic, anionic, non-ionic and amphoteric. The best results in terms of improved delignification, lower screen rejects and lighter coloured unbleached pulps were obtained with the non-ionic surfactants. When compared with the reference, these cooks exhibited a decrease of up to 6.2% in Kappa number and 39% in screen rejects, and up to a 9% increase in the unbleached pulps reflectance factor. The most promising surfactants in terms of reflectance factor were poly(ethyleneglycol) 1000-4%, block copolymer poly(ethyleneglycol) - poly(propyleneglycol) 1100-4% and poly(oxyethylene) 100 stearyl ether-1%. It was also established that the use of surfactants as cooking additives did not influence the bleachability, but allowed savings of chlorine dioxide in the first bleaching stage (about 5.2%), with consequent environmental and economical benefits.

Keywords
Pinus pinaster, kraft pulp, surfactants, Kappa number, reflectance factor, screen rejects, bleachability

Pinus pinaster (maritime pine) is the most important Portuguese forest species (32% of the forest land), and around 16% is used for unbleached kraft pulp production. This pulp shows systematically lower optical properties. In fact, it is more coloured and has poor bleachability when compared with other softwood pulps. The efforts of our research group have been focused on understanding the origin of these negative aspects and trying to solve them. In all cases, our main objective is to better understand chemical changes in lignin structure during delignification, both in residual and dissolved lignins (*1-3*). Our previous studies were devoted to three research directions, namely (i) the use of a wood chips pretreatment to improve the pulp quality, e.g. carbohydrate degrading enzymes (*4,5*), alkaline extraction (*6,7*) and organic solvents extractions (*6,7*); (ii) cooking using a flow-through reactor to minimise lignin condensation reactions (*1,2*); and (iii) conventional cooking in the presence of different surfactants to minimise the deposition of thermally degraded substances on the fibre surface, thus preventing dark coloration (*6,7*).

The use of surfactants as cooking additives minimises the surface tension between the liquor and the chips, allowing the wetting of chip surfaces. Some results have already been obtained with the surfactant technology, giving rise to more uniform cooking with lower Kappa numbers, lower screen rejects, lower pulp resin content and improved black liquor residual active alkali content (*8-10*). Some other studies showed that the products of thermal degradation of extractives were strongly coloured and could contribute to the dark colour of unbleached pulps (*11,12*). This suggests another possibility of surfactant action, which is to avoid the deposition of the extractive degradation products onto the surface of fibres (*7*).

The present work is mainly based on the use of different surfactants from four different families, namely: cationic, anionic, non-ionic and amphoteric, and 17 surfactants were used in about 70 cooks performed with the same kraft conditions. The yield, screen rejects, Kappa number, degree of polymerisation (DP) and reflectance factor (ISO%) of the resultant pulps were characterised by common standards. The bleachability of the most promising samples in terms of reflectance factor was analysed in order to ascertain its bleaching response using a short bleaching sequence (DE). The bleachability of these pulps was compared with a reference pulp obtained using the same kraft conditions but without surfactant.

EXPERIMENTAL

Material

The *Pinus pinaster* wood chips were obtained from a commercial kraft mill and were manually classified as homogeneous as possible with a size of about 20x12x2 mm. The surfactants used were from four different families – cationic, anionic, non-ionic and amphoteric with low and high molecular masses (Table 1). They were commercial products of the highest purity available, supplied by Aldrich Co.

Pulping

The first set of pulping experiments was carried out in laboratory mini-digesters having a capacity of 200 mL. The wood was cooked in the presence of the different surfactants at different concentrations (see Table 1). A control sample was also produced simultaneously without surfactant addition (sample R). All the experiments were performed at least twice.

The pulping conditions were as follows: active alkali, 21% (as NaOH); sulfidity, 30%; temperature, 2 hours from ambient to 170°C and 1 hour 47 minutes at 170°C; H factor, 1800; liquor to wood ratio, 5:1. After cooking the chips were extensively washed and screened on an L & W laboratory screen.

Bleaching

Bleaching experiments were carried out with a short bleaching sequence (DE), corresponding to an oxidation stage with chlorine dioxide and an alkaline extraction stage, respectively, in sealed plastic bags in a shaking water bath.

The bleaching conditions were: (1) D stage – ClO_2 charge (%), 0.2xKappa number/2.63; temperature, 70°C; stock concentration, 10%; reaction time, 2 hours; initial pH, 2: (2) E stage – NaOH charge (%), $^1/_2$ of the active chlorine charge used in D stage; temperature, 70°C; stock concentration, 10%; reaction time, 1 hour.

* Assistant Professor, Polytechnic Institute of Tomar, High Technological School, Department of Chemical Engineering, 2300 Tomar, Portugal.
† Professor, EFPG/INPG, BP65, 38402 Saint Martin d'Hères Cedex, France.
‡ Associate Professor, Department of Paper Science and Technology, University of Beira Interior, 6201-001 Covilhã, Portugal. Author for correspondence, email: apduarte@ciunix.ubi.pt

Table 1
Results of the various surfactant treatments.

Type of surfactant		Surfactant concentration, %[a]	Screened yield, %	Screen rejects, %	Black liquor RAA[b], g/L	Kappa number	Pulp reflectance factor, % ISO
R	–	–	41.6	6.2	5.15	50.0	24.0
Cationic	1,3-didecyl-2-methylimidazolium chloride, 97%	1	36.8	8.8	5.13	54.3	18.5
		4	45.2	10.9	3.95	nd[c]	18.0
	Hexadecyltrimethyl ammonium bromide	1	41.4	2.7	4.86	57.6	19.5
		4	40.9	5.2	4.93	nd	18.0
		6	44.4	3.5	5.85	nd	18.2
Anionic	Dodecyl sulfate, sodium salt 98%	1	43.6	4.2	4.70	57.7	22.3
		4	35.4	11.9	4.26	nd	21.4
		6	46.4	1.1	5.10	nd	21.3
	Poly(ethyleneglycol)4-noylphenyl-3-sulfopropylether, potassium salt	1	40.5	5.3	4.98	nd	20.6
		4	40.9	4.6	4.97	46.7	22.3
		6	44.6	1.4	4.80	nd	19.0
	Calcium stearate	1	nd	nd	nd	48.2	23.2
		4	nd	nd	nd	nd	21.2
Amphoteric	N,N-dimethyl-N-[3-(sulfooxy)-propyl]-1-decanaminium hydroxyde, inner salt	1	40.6	6.2	4.45	50.9	18.1
		4	31.1	16.7	4.03	nd	16.9
Non-ionic	Poly(ethyleneglycol) 400	1	nd	nd	nd	nd	23.4
		4	nd	nd	nd	49.8	24.2
	Poly(ethyleneglycol) 1000	1	nd	nd	nd	48.7	24.5
		4 **(S1)**	41.8	4.3	3.39	47.8	26.1
		6	nd	nd	nd	45.0	24.2
	Poly(ethyleneglycol) 1500	1	40.9	4.8	3.57	48.8	23.6
	Poly(ethyleneglycol) 4000	1	42.2	4.6	5.19	50.8	24.1
	Poly(ethyleneglycol) 10 000	4	nd	nd	nd	43.7	24.9
		6	nd	nd	nd	43.6	24.4
	Poly(propyleneglycol) 11 000	1	nd	nd	nd	47.4	24.0
	Block copolymer poly(ethyleneglycol)-poly(propylene glycol) 1100	1	nd	nd	nd	50.3	23.9
		4 **(S2)**	40.9	4.8	nd	46.9	25.3
		6	nd	nd	nd	52.9	22.4
	Poly(oxyethylene) 100 000	1	nd	nd	5.41	50.4	23.4
	Poly(oxyethylene) 8 000 000	1	---	---	5.39	---	---
	Poly(oxyethylene 10 stearyl ether)	1	nd	nd	6.28	48.0	24.9
	Poly(oxyethylene 100 stearyl ether)	1 **(S3)**	42.0	3.8	6.14	47.5	25.2
		4	nd	nd	nd	46.1	24.3

[a] on o.d. wood basis; [b] residual active alkali; [c] not determined.

Pulp characterisation

The Kappa number and intrinsic viscosity of the pulps were determined according to ISO 302-1981 and ISO 5351/1-1981, respectively. The DP was calculated using the equation proposed in SCAN-C15:62, $DP^{0.905} = 0.75*[\eta]$. The pulp handsheets were prepared according to ISO 5269/1-1979, except for the drying procedure. In the present work the handsheets were immediately dried in an L & W rapid dryer for laboratory sheets. The ISO reflectance factor of pulp handsheets was measured using an abridged spectrophotometer, Color Touch 2 Model ISO, from Technidyne Corp. according to ISO 2470-1977.

RESULTS AND DISCUSSION

Pulping

A set of pulp experiments was performed

Table 2
Relative error for the different determinations.

	Screened yield, %	Screen rejects, %	Black liquor RAA[b], g/L	Kappa number	Pulp reflectance factor, % ISO
Relative error, %	2.92	8.05	3.34	1.20	3.52

with the same pulping conditions using different surfactants at different concentrations. The effect of these surfactant treatments on pulp delignification, pulp yield and screen rejects, black liquor residual alkali content and pulp handsheet reflectance factor are given in Table 1.

In order to have an indication of the reproducibility of the cooking experiments the relative error of each pulp characteristic was calculated from the duplicate cooks (see Table 2).

The Kappa number results given in Table 1 show that most of the surfactant treatments produced higher delignification levels when compared with the reference. The highest performances were obtained when using non-ionic surfactants, namely poly(ethyleneglycol) 1000 – 4% (**S1**), block copolymer of poly(ethyleneglycol)-poly(propylene glycol) 1100 – 4% (**S2**) and poly(oxyethylene 100 stearyl ether) – 1% (**S3**). The higher delignification of the wood chips could also be because surfactants can act as a co-solvent capable of swelling and consequently facilitating liquor penetration into wood pores. These trials also produced less coloured pulps with higher reflectance factors, which was the principal objective of this work. Thus, the reflectance factor was the elected characteristic to determine the effectiveness of surfactant treatment on kraft pulping and to select the samples for further studies.

As observed above, the non-ionic surfactants showed the best results in terms of reflectance factor. These surfactants are known to minimising the production of foam, which can be beneficial due to the process and environmental concerns with excessive foam.

The optimum surfactant concentration level is rather high, which is probably because cooking is carried out at high temperature (170°C), which is known to decrease the efficiency of surfactants by increasing their solubility (*13*).

The molecular mass of the non-ionic surfactant was also varied from 400 to 8,000,000. The results obtained showed that there is a maximum performance at a molecular mass of about 1000, which gives the highest gains in the reflectance factor (see S1, S2 and S3). According to the literature, the non-ionic surfactant molecular mass should be higher than 100,000 for good efficiency (*13*), which suggests that the performances obtained are probably due to the co-solvent effect of the surfactants. Indeed, it was observed that the poly(oxyethylene) 100,000 did not improve the reflectance factor relative to the reference. Furthermore, the poly(oxyethylene) 8,000,000 impeded the washing of the pulp.

Another feature observed with these treatments is the lower screen rejects content obtained in almost all experiments, which could indicate a more uniform penetration of cooking chemicals giving rise to more homogenous wood pulping, which is in agreement with other studies (*8-10*).

The most promising pulps (**S1**, **S2** and **S3**) were chosen to perform bleachability studies. In these pulping experiments it was observed that the presence of surfactants in the pulping process increased the delignification by up to 6.2% due to the enhanced wetting properties. Consequently, the pulp reflectance factor was improved and in this case the gain was about 9%. These 3 pulping experiments also had lower screen rejects than that obtained in the reference experiment (Fig. 1). It is worth noting that experiment **S3** showed the best result with a 39% decrease in rejects content.

The pulping experiment **S3** also exhibited higher black liquor residual active alkali content when compared with the experiment without surfactant, suggesting a lower consumption of chemicals, even though the delignification level was higher and the screen rejects content lower. This indicates that the use of Poly(oxyethylene 100 stearyl ether) could allow a reduction in the alkali charge to the digester, with the inherent process benefits.

Concerning the cellulose degradation of these pulps, the degree of polymerisation (DP) results are presented in Figure 2.

Figure 2 shows that the presence of these surfactants gives a decrease in cellulose degradation, probably by enhancement of the selectivity of the delignification process as shown in Figure 3, which is in agreement with other literature data concerning similar experiments with low molecular mass Poly(ethyleneglycol) (*14*). This observed cellulose DP increase relative to the reference was not reflected in the screened pulp yields.

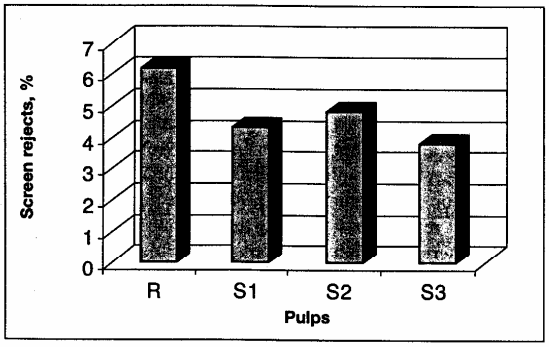

Fig. 1 Screen rejects of the selected pulps and reference.

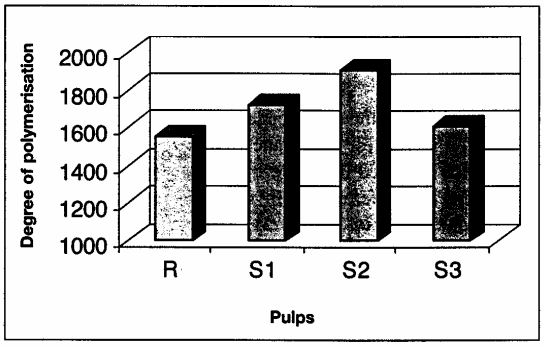

Fig. 2 Degree of polymerisation of the selected pulps and of the reference.

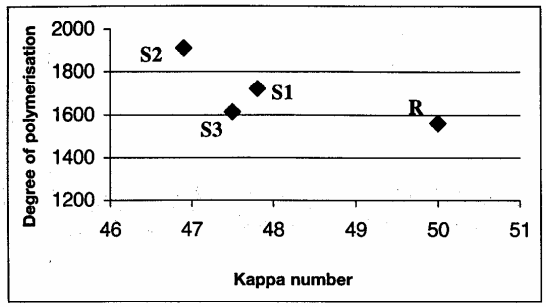

Fig. 3 Degree of polymerisation versus Kappa number of the selected pulps.

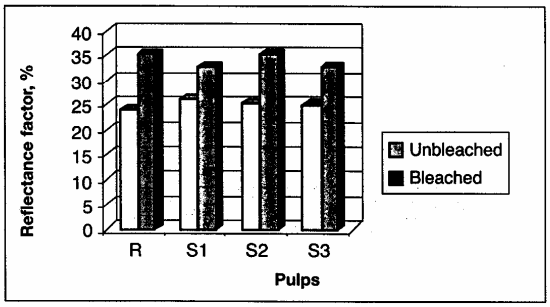

Fig. 4 Reflectance factor of unbleached and bleached pulps.

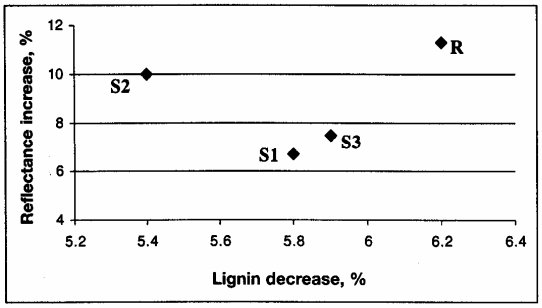

Fig. 5 Reflectance increase versus lignin decrease in DE bleaching.

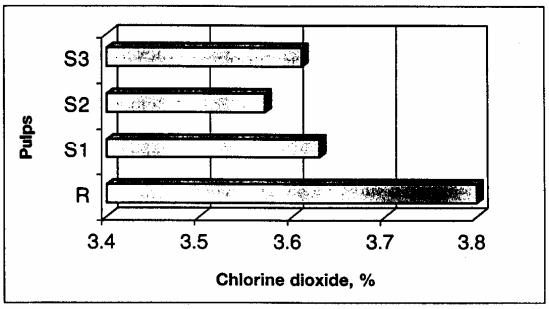

Fig. 6 Amount of chlorine dioxide used in the D stage.

This occurrence could be explained by the increased delignification obtained in those experiments (see Kappa numbers), which masks any yield improvement.

Bleaching

The objective of this part of the work was to establish the influence of the presence of the selected surfactants on pulp bleachability. For this purpose a methodology was chosen based on a short sequence commonly proposed in the literature, i.e. two bleaching stages – DE.

The comparison between the reflectance factor of the unbleached and the bleached pulps is given in Figure 4.

As can be seen, the bleachability of the pulps tested is not improved by the presence of surfactant during cooking, since the reference pulp achieved the highest reflectance. This fact is also observed in Figure 5, which shows that the reference pulp reached the highest ratio of reflectance increment/lignin reduction.

Nevertheless, as the Kappa number of the unbleached pulp is lower, the amount of chemicals used in bleaching is consequently lower, which represents a good saving for the industrial process. Figure 6 shows that the amount of chlorine dioxide used for each pulp, with the higher quantity required for the reference pulp as expected since it is proportional to the pulp Kappa number. It is noteworthy that the chlorine dioxide residuals for the D stage were in the range of 0.0008 and 0.0014%, which is negligible and indicative of full chemical consumption.

CONCLUSIONS

This work constitutes a study on the effect of surfactants as cooking additives for the improvement of optical characteristics and bleaching response of unbleached pulps from *Pinus pinaster*. From these experiments it can be concluded that the presence of surfactants as cooking additives improves the delignification process, giving rise to the production of pulps with lower Kappa number, higher DP, and higher reflectance factors, which are important parameters for the unbleached pulp industry. The results with the surfactant treatments, in terms of screen rejects content and black liquor residual active alkali content, indicate better penetration and diffusion of the cooking liquor and a more effective use of cooking chemicals.

Surfactant treatment did not give any improvement in pulp bleachability, but the use of surfactants diminished the amount of bleaching chemicals required, which could be considered as beneficial from the environmental and economic points of view.

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Table 5
Theoretical cleaning efficiency for the two deinking lines.

Stage	Theoretical cleaning efficiency based on stage removable flakes (%)	Stage	Total theoretical cleaning efficiency based on total removable flakes (%)
F_1^{th}(A-B)S.R	46.1	F_1^{th}(A-B)T.R	40.2
F_1^{th}(B-C)S.R	63.5	F_1^{th}(B-C)T.R	34.5
F_1^{th}(C-D)S.R	56.9	F_1^{th}(C-D)T.R	14.5
F_1^{th}(A-D)S.R	89.1	F_1^{th}(A-D)T.R	89.1
F_2^{th}(A-B)S.R	42.3	F_2^{th}(A-B)T.R	38.4
F_2^{th}(B-C)S.R	74.5	F_2^{th}(B-C)T.R	44.8
F_2^{th}(C-D)S.R	55.3	F_2^{th}(C-D)T.R	9.3
F_2^{th}(A-D)S.R	92.5	F_2^{th}(A-D)T.R	92.5

Note: S.R. – 'Stage Removable Flakes'
T.R. – 'Total Removable Flakes'

Table 6
Actual cleaning rate for the two deinking lines.

Stage	Actual cleaning rate based on stage entrance flakes (%)	Stage	Total actual cleaning rate based on total entrance flakes (%)
F_1^{ac}(A-B)S.E.	48.7	F_1^{ac}(A-B)T.E.	48.7
F_1^{ac}(B-C)S.E.	49.2	F_1^{ac}(B-C)T.E.	25.2
F_1^{ac}(C-D)S.E.	62.6	F_1^{ac}(C-D)T.E.	16.3
F_1^{ac}(A-D)S.E.	90.2	F_1^{ac}(A-D)T.E.	90.2
F_2^{ac}(A-B)S.E.	53.1	F_2^{ac}(A-B)T.E.	53.1
F_2^{ac}(B-C)S.E.	73.0	F_2^{ac}(B-C)T.E.	34.2
F_2^{ac}(C-D)S.E.	67.3	F_2^{ac}(C-D)T.E.	8.5
F_2^{ac}(A-D)S.E.	95.8	F_2^{ac}(A-D)T.E.	95.8

Note: S.E. – 'Stage Entering Flakes'
T.E. – 'Total Entering Flakes'

CONCLUSIONS

The performance of the two deinking lines at the Guangzhou Paper Mill was benchmarked for removal of ink and flakes and the deinking efficiency, deinking rate, cleaning efficiency and cleaning rate were calculated. Analysis of the results suggests that the actual and total actual deinking rates, and the actual and total actual cleaning rates, are useful tools to evaluate the working efficiency in deinking lines and to compare differences in performance between deinking lines.

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