

## APPLICATION OF SURFACTANTS AS PULPING ADDITIVES IN SODA PULPING OF BAGASSE

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The effects of several non-ionic commercial surfactants and their dosage on soda pulping and ECF bleaching of soda and soda-surfactant pulps of bagasse were investigated. The properties of bleachable pulps obtained with conventional soda and with soda-surfactants were studied and compared. The results showed application of surfactants during the soda pulping of bagasse decreased kappa number and improved the yield and brightness of resulting pulp. Using the surfactants reduced alkali consumption during pulping. The bleaching experiments showed that the pulps obtained with the three types of applied surfactants namely, ELA-2, FAE-20, and PEG1000 could be easily bleached with  $D_0ED_1$  or  $D_0EpD_1$  sequences. The addition of most used surfactants in soda pulping of bagasse led to higher brightness in comparison to reference pulp with the same bleaching sequence. Strength properties of bleached pulps obtained with surfactants were higher than the pulp obtained with conventional soda pulping.

*Keywords:* Non-Wood; Bagasse; Soda Pulping; Additives; Non-ionic Surfactant; ECF Bleaching

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### INTRODUCTION

Bagasse, the sugarcane residue after sugar extraction, is one of the most available papermaking lignocellulosic fiber resources in some developing countries, e.g., Iran. Approximately 4.3 million tons of bagasse is produced annually in Iran that is mainly centered in the southwestern province of Khuzestan (Najafi et al. 2009). Soda pulping is traditionally the most employed chemical pulping process for various non-wood raw materials including bagasse (Khristova et al. 2006; Enayati et al. 2009). However, the soda pulping of non-woods produces a low yield and highly colored pulp, consuming a large amount of bleaching chemicals (Francis et al. 2006; Labid et al. 2008). Some drawbacks of soda pulping could be overcome by the using of suitable pulping additives. The addition of anthraquinone (AQ) to soda pulping liquor is known as an effective and simple approach that increases delignification selectivity, carbohydrate protection, and pulp yield. On the other hand, anthraquinone is an expensive material, and produced alkali-AQ pulps have lower bleachability (Khristova et al. 2005; Francis et al. 2006; Francis et al. 2008; Jahan et al. 2008) and lower tear strength compared to conventional soda pulp (Khristova et al. 1998; Francis et al. 2006). Moreover, very fine powder of anthraquinone is an environmental nuisance if it is not handled properly and in soda pulping operations without recovery systems applied anthraquinone is released into the environment.

Several studies have been performed aiming to find alternative cost effective pulping additives without causing adverse effects on pulping and bleaching (Kosikova and Mlynar 1992; Tanczos and Harald 2002; Sarwar Jahan et al. 2004; Francis et al. 2006; Jiménez et al. 2009).

Previous studies have shown that addition of 0.5 to 1% of surfactants to cooking liquor of kraft pulping of hardwood and softwood species, in laboratory and industrial scales resulted in more uniform pulps with lower rejects, higher pulp yield at constant kappa number, and lower consumption of alkali (Duggiralla 2000). Similar results have been reported by Baptista et al. (2004), in kraft pulping of *Pinus pinaster* using non-ionic surfactants. Several types of surfactants have been investigated in these studies, and the better results were obtained with the non-ionic surfactants compared to cationic, anionic, and amphoteric surfactants. According to Baptista et al. (2004), non-ionic surfactants have other advantage, since they can be used as anti-foam agents. Recently, Duggirala et al. (2002) indicated that addition of alkyl alcohol alkoxyate surfactant in the kraft pulping reduced resin content of pulp after cooking and washing stages.

Guo et al. (2002), showed that alkaline pulping of a mixture of hardwood species in a bi-phasic system containing PEG-1000 and kraft cooking chemicals resulted in faster delignification, higher delignification selectivity, and 10 to 20 % higher yield at similar kappa number, compared to conventional kraft cooking. They have considered that addition of PEG to kraft cooking liquor decreases the activation energy of delignification and hydrolysis of cellulose and hemicelluloses (Guo et al. 2002; Guo et al. 2003a).

In addition, it has been recently revealed that the addition of surfactants into pulping liquor has several advantages, e.g., reducing the pollution load of bleaching effluents in term of COD, chloride, and dissolved solids (Mishra et al. 2007).

Chen and co-workers (2002) reported that employing commercial ethoxy-based alcohol surfactants accelerated oxygen delignification of softwood kraft pulp, without any adverse impact on the selectivity of the delignification.

According to Ehara et al. (2000), some nonionic surfactants effectively improved the brightness of pulp with manganese peroxidase (MnP) biobleaching. They suggested that these surfactants probably accelerated dispersion of the hydrophobic degraded lignin from the pulp into buffer solution during MnP treatment.

Although addition of surfactants has shown several beneficial effects on the pulping properties of softwoods and hardwoods, very limited information is available on the use of surfactants as pulping additives for soda pulping of non-wood fibers, which produces a low yield and highly colored pulp. Therefore, the present study reports the effect of several non-ionic surfactants and their dosage on the soda pulping and ECF bleaching of bagasse.

## EXPERIMENTAL

The depithed bagasse used in this study was collected from a local pulp and paper mill (Pars Paper Co. Haft Tapeh. Iran). The  $\alpha$ -cellulose, lignin, ash and ethanol/acetone extractable of bagasse were determined according to TAPPI Test Methods. The holocellulose and cellulose content of bagasse were determined according to the Wise

(1946) and nitric acid (Rowell and Young 1997) methods, respectively. The hemicelluloses contents of bagasse were calculated by decreasing of cellulose content from holocellulose. The chemical composition of depithed bagasse i.e., holocellulose, cellulose,  $\alpha$ -cellulose, lignin, ash, and ethanol/acetone extractables, was determined as 74.9%, 54.3%, 45.3%, 21.4%, 2.64%, and 1.6% on an oven-dry weight basis, respectively.

Before pulping, bagasse was washed, depithed and air-dried. The conventional soda pulping of bagasse was carried out as the reference cook with 15% active alkali (as NaOH) based on the dry weight of bagasse at 165°C for 60 min. Under the same pulping conditions, the modified cooks were performed with various commercial non-ionic surfactants, including PEG400, PEG1000, lauryl alcohol ethoxylated with 2 moles ethylene oxide per mole of alcohol (ELA-2), lauryl alcohol ethoxylated with 7 moles ethylene oxide per mole of alcohol (ELA-7), lauryl alcohol ethoxylated with 20 moles ethylene oxide per mole of alcohol (ELA-20), nonylphenol ethoxylated with 4 moles ethylene oxide per mole of nonylphenol (ENP-4), and fatty amine ethoxylated with 20 moles ethylene oxide per mole of fatty amine (FAE-20). Modified cooks were performed by adding 1% and 4% (weight percentage) of each surfactant based on the dry weight of bagasse into soda pulping liquor. Pulping experiments were carried out with 100 g of o.d. bagasse using a 1L thermostatic oil-heated multi-batch digester. After cooking, the black liquors were analyzed for residual alkali, and the resulting pulps were washed and then screened on a 100 mesh slot screen. The screen yield and rejects were determined as percentage of oven-dry bagasse. The kappa number and freeness of the accepted pulps were determined according to TAPPI T 236 om-85 and T 227 om-99 Test Method, respectively. In order to have an estimation of the reproducibility of pulping experiments, all cooks were performed two times, and the relative error of pulp properties was less than 3.9%.

The reference pulp and optimum pulps with different surfactants were then bleached in a three-stage D<sub>0</sub>ED<sub>1</sub> or D<sub>0</sub>EpD<sub>1</sub> bleaching sequence. The D<sub>0</sub> stage (ClO<sub>2</sub> delignification stage) was performed at 70 °C for 60 min. The ClO<sub>2</sub> charge in the D<sub>0</sub> stage of D<sub>0</sub>ED<sub>1</sub> and D<sub>0</sub>EpD<sub>1</sub> sequences were 1.1% and 1% respectively. The alkaline extraction stage was done at 70 °C for 60 minutes with 1.2% NaOH charge for conventional E stage and a charge of 1% NaOH, 0.2% H<sub>2</sub>O<sub>2</sub> for peroxide reinforced extraction Ep stage. The temperature in the D<sub>1</sub> stage (ClO<sub>2</sub> bleaching stage) was 80 °C for 80 min. The ClO<sub>2</sub> charges in the D<sub>1</sub> stage of D<sub>0</sub>ED<sub>1</sub> and D<sub>0</sub>EpD<sub>1</sub> sequences were 0.8% and 0.65%, respectively.

Standard hand sheets (60 g/m<sup>2</sup>) were made from bleached pulps without refining according to TAPPI T 205 om-88. The paper sheets were conditioned at 23 °C and 50% R.H. for 24 hours. Then, the brightness of the bleached pulps was determined in accordance with TAPPI T-452 om-98 Test Method, using a Technibrite Micro TB-1C Spectrophotometer. The breaking length, burst index, and tear index of paper sheets were determined according to TAPPI T 494 om-88, T 403 om-97, and T414 om-98 Test Method, respectively.

## RESULTS AND DISCUSSION

### Pulping Results

Table 1 compares the effect of various surfactants and their concentration on the pulp properties. Addition of surfactants to pulping liquor resulted in pulps with lower kappa number (except for PEG400 and ENP-4), lower screen rejects, and higher brightness compared to the control pulp.

Moreover, alkali consumption in pulping with surfactants was reduced in all the trials. These results are in agreement with other studies applying surfactants as pulping additives (Duggiralla, 2000; Baptista et al. 2004). In the most cases, with the increased amount of surfactants, the pulping yield and delignification rate decreased. In other words, the optimum dosage of surfactants was 1% except for PEG1000, with higher yield and lower kappa number obtained with 4% surfactant. In the case of PEG1000, one explanation could be that the higher dosage of PEG-1000 improves phase separation of a bi-phasic system, which in turn increases lignin dissolution in the polymer-phase and decreases lignin condensation, resulting in lower kappa number (Guo et al. 2003b).

**Table 1.** Effects of Various Surfactants on Soda Pulping of Bagasse

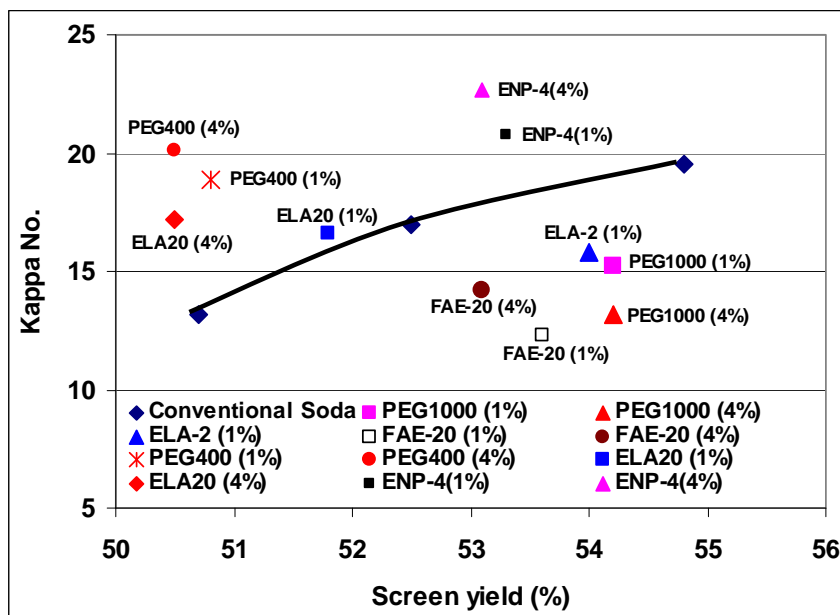
| Surfactant   |   | Yield (%) |        | RAA (%) | Kappa No. | Brightness (%) |
|--------------|---|-----------|--------|---------|-----------|----------------|
| Type         | % | Screen    | Reject |         |           |                |
| Soda-Control | 0 | 52.5      | 1.1    | 3.9     | 17.1      | 36             |
| PEG400       | 1 | 50.8      | 0.4    | 3.8     | 18.9      | 37             |
|              | 4 | 50.5      | 0.8    | 4.0     | 20.1      | 38             |
| PEG1000      | 1 | 52.4      | 0.4    | 7.9     | 15.2      | 38             |
|              | 4 | 54.2      | 0.3    | 7.9     | 13.2      | 38             |
| ELA-2        | 1 | 54.0      | 0.5    | 8.2     | 15.8      | 41             |
|              | 4 | 51.2      | 0.9    | 5.3     | 16.3      | 42             |
| ELA-7        | 1 | 51.7      | 0.4    | 6.4     | 14.4      | 40             |
|              | 4 | 50.9      | 0.3    | 6.3     | 15.3      | 39             |
| ELA-20       | 1 | 51.8      | 0.5    | 5.3     | 16.6      | 38             |
|              | 4 | 50.5      | 0.3    | 6.8     | 17.2      | 38             |
| ENP-4        | 1 | 53.3      | 0.61   | 6.4     | 20.8      | 38             |
|              | 4 | 53.1      | 0.67   | 8.4     | 22.7      | 38             |
| FAE-20       | 1 | 53.6      | 0.5    | 5.8     | 12.3      | 41             |
|              | 4 | 53.1      | 0.2    | 6.2     | 14.2      | 40             |

\* RAA: Residual Active Alkali

Comparison of the pulps obtained with the different surfactants showed that PEG1000 (4%), ELA-2 (1%), and FAE-20 (1%) improved the selectivity of delignification and produced the best pulps, with higher yield and lower kappa number compared to the conventionally produced soda pulp (Fig. 1). Application of surfactants as pulping additives decreases surface tension between the cooking liquor and lignocellulosic materials, resulting in faster liquor penetration and more uniform cooking with lower kappa and lower rejects (Duggiralla, 2000; Baptista et al. 2004; Mishra et al. 2007). Based on these suggestions, the positive effects of surfactants on pulping of hardwoods and softwoods have been attributed to the higher penetration of cooking

liquor in the wood chips, extraction of wood extractives, and avoiding the deposition of extractive degradation products on to the surface of fibers.

However, considering the bulk density of bagasse, the observed positive effects of some surfactants on the soda pulping of bagasse cannot be explained only as an effect of increasing the cooking liquor penetration. Perhaps, surfactants act as a co-solvent and change the properties of soda cooking liquor, inhibiting the degradation of carbohydrates, decreasing the lignin reprecipitation on the fiber, and decreasing condensation reactions of lignin (Guo et al. 2003; Baptista et al. 2006; Baptista et al. 2006). This suggestion could be supported by results from another study where the carbohydrates protection effect of surfactants has been confirmed in the eucalyptus globulus kraft pulping with 0.25% addition of an alcohol derivative surfactant into kraft liquor, which resulted in higher pulp viscosity (Santiago et al. 2008). Furthermore, analysis of residual lignin after kraft cooking of *Maritime pine* have revealed that addition of PEG1000 to cooking liquor decreased the amount of condensed structures in residual lignin (Baptista et al. 2006). Thus, the higher pulp yield at lower kappa number obtained due to the addition of PEG1000 (4%), ELA-2 (1%) and FAE-20 (1%) to soda pulping liquor, could be attributed to the synergistic effects of carbohydrates protection and decreasing lignin condensation reactions.



**Fig. 1.** Screen yield versus kappa number for conventional soda pulping of bagasse and for soda pulping of bagasse with various surfactants.

## Bleaching Results

The pulps obtained from conventional soda pulping and from the cooks containing the most effective surfactants, i.e., 1% ELA-2, 1% FAE-20, and 4% of PEG1000 were selected to evaluate the effects of surfactants on the bleachability of pulps. The results in Table 2 show the effects of the applied surfactants on the bleaching response of the pulps in the DED and DEpD bleaching sequences. Application of

surfactants not only increased the unbleached pulps brightness but also improved bleachability of the pulps. The pulps obtained from 1% ELA-2, 1% FAE-20, and 4% PEG1000 showed higher brightness degree than that of the conventional soda pulp. This can be explained by the lower initial kappa number and higher unbleached brightness. As seen in Table 2, compared to DED sequence, higher brightness was obtained with DEpD sequence due the hydrogen peroxide action in lignin oxidation and degradation of chromophoric structures.

**Table 2.** Bleaching Results of Selected Pulps by D<sub>0</sub>ED<sub>1</sub> / D<sub>0</sub>EpD<sub>1</sub> Sequence

| Pulping           | Unbleached pulp |                | Bleaching sequence | DE/DEp bleached pulp |                | DED/DEpD Brightness (%) |
|-------------------|-----------------|----------------|--------------------|----------------------|----------------|-------------------------|
|                   | Kappa No.       | Brightness (%) |                    | Kappa No.            | Brightness (%) |                         |
| Conventional soda | 17.1            | 36             | DED                | 3.9                  | 48.9           | 66.2                    |
|                   |                 |                | DEpD               | 3.2                  | 53.0           | 67                      |
| 1% ELA-2          | 15.9            | 41             | DED                | 3.1                  | 50.0           | 68.3                    |
|                   |                 |                | DEpD               | 2.7                  | 59.0           | 69.5                    |
| 1% FAE-20         | 12.3            | 41             | DED                | 2.0                  | 52.0           | 70.6                    |
|                   |                 |                | DEpD               | 1.9                  | 61.1           | 72.6                    |
| 4% PEG1000        | 13.2            | 38             | DED                | 2.0                  | 54.0           | 69.8                    |
|                   |                 |                | DEpD               | 1.9                  | 59.8           | 71.3                    |

### Strength Properties of the Unbleached, DED Bleached and DEpD Bleached Pulps

Table 3 shows the strength properties of unbleached, DED bleached and DEpD bleached pulps prepared with different pulping conditions.

**Table 3.** Freeness, Burst Index, Tear Index, and Tensile Index of Unbleached and Bleached Pulps Obtained Without Surfactant and with Different Surfactants

| Pulp                | Type         | % | CSF Freeness (ml) | Burst Index (kPa.m <sup>2</sup> /g) | Tear Index (mN.m <sup>2</sup> /g) | Tensile index (Nm/g) |
|---------------------|--------------|---|-------------------|-------------------------------------|-----------------------------------|----------------------|
| Unbleached pulps    | Soda-Control | 0 | 690               | 2.19                                | 4.50                              | 47.66                |
|                     | PEG1000      | 4 | 720               | 2.50                                | 4.56                              | 54.28                |
|                     | ELA-7        | 1 | 720               | 2.67                                | 5.25                              | 49.34                |
|                     | ELA-2        | 1 | 710               | 2.67                                | 4.60                              | 49.34                |
|                     | FAE-20       | 1 | 700               | 2.46                                | 4.58                              | 50.02                |
| DED bleached pulps  | Soda-Control | 0 | 690               | 2.71                                | 5.73                              | 49.46                |
|                     | PEG1000      | 4 | 680               | 2.99                                | 6.13                              | 55.69                |
|                     | ELA-7        | 1 | 700               | 2.92                                | 6.95                              | 51.73                |
|                     | ELA-2        | 1 | 700               | 2.81                                | 6.13                              | 50.54                |
|                     | FAE-20       | 1 | 690               | 3.09                                | 6.19                              | 51.21                |
| DEpD bleached pulps | Soda-Control | 0 | 690               | 2.96                                | 6.13                              | 51.55                |
|                     | PEG1000      | 4 | 710               | 3.25                                | 6.27                              | 55.47                |
|                     | ELA-7        | 1 | 680               | 3.23                                | 7.22                              | 52.24                |
|                     | ELA-2        | 1 | 670               | 3.33                                | 6.24                              | 53.77                |
|                     | FAE-20       | 1 | 680               | 3.40                                | 6.15                              | 54.87                |

Addition of surfactants caused an increase in the burst, tear, and tensile strengths of the pulp. This may be attributed to the higher flexibility of pulp fibers produced from surfactant containing cooks with higher degree of delignification. A more delignified fiber is more porous and is known to have higher flexibility and higher specific surface area. These changes, in turn, lead to higher strengths (Risen et al. 2004). Unbleached pulps exhibited the lowest strength and after the DED bleaching sequence; the strength properties of pulps increased. The DEpD bleached pulps showed the highest strengths. A possible explanation is that the unrefined fiber of bagasse pulp becomes more porous, when much lignin and carbohydrates are removed during bleaching. This increases the surface area and flexibility of fibers, which in turn leads to denser paper with higher strength properties.

## CONCLUSIONS

This study provides the following conclusions:

1. The addition of some non-ionic surfactants as cooking additive of soda pulping of bagasse provided higher yield, lower kappa (except for PEG400 and ENP-4), and brighter pulps than the conventional soda pulp. The addition of all studied surfactants reduced active alkali consumption.
2. Out of the five surfactants employed in this study, the best results were obtained with 1% ELA-2, 1% FAE-20, and 4% PEG1000, with 1-1.5% higher screen yield and about 4 points lower kappa number.
3. The bleaching of pulps in the DED or DEpD bleaching sequences showed that the pulps obtained using 1% ELA-2, 1% FAE-20, and 4% PEG1000 achieved higher brightness than that of the conventional soda pulp.
4. The overall results of this study indicated a high potential of the added surfactants to improve the pulp quality and reduce the adverse environmental impacts of bagasse-soda pulping and bleaching.

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