THE EFFECT OF SURFACTANTS APPLICATION ON SODA PULPING OF WHEAT STRAW

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This paper details the effects of two non-ionic surfactants, ELA-7 and PEG 1500, on the soda pulping of wheat straw. The results showed that application of either surfactant improved the pulp yield and decreased the screen rejects. The increase in pulp yield at similar kappa number may be due to higher selectivity of delignification affected by surfactant, which can act as a co-solvent. Addition of ELA-7 to cooking liquor didn't have significant effect on paper properties. But a significant effect was observed with PEG 1500. In fact, it caused a decrease in burst and tensile index but increased the tear index, probably because of a debonding effect of the surfactant. In addition, application of both surfactants improved brightness for both unbleached and bleached pulp samples.

Key words: Wheat Straw; Soda Pulping; Non-ionic Surfactant; PEG 1500; ELA-7; Yield

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INTRODUCTION

The use of surfactants as cooking additives minimizes the surface tension between the liquor and chips, resulting in wetting of the chips' surfaces. This gives rise to more uniform cooking with lower kappa number, lower screen rejects, lower resin content, and improved black liquor residual active alkali (Dugiralla 1999, 2000). The products of thermal degradation of extractives are strongly colored and contribute to the dark color of unbleached pulps (Forsskahl 1992; Forsskahl et al. 1998). These results suggest another possibility of surfactant action, which is to avoid the deposition of extractive degradation products on to the surfaces of fibers. In conventional cooking, the presence of different surfactants minimizes the deposition of thermally degraded substances of the fiber surface, thus preventing dark colouration (Baptista et al. 1999, 1999). The removal of extractives also contributes to a decrease in kappa number, because these are the compounds that are oxidizable by the permanganate solution used in kappa determination (Ala-kail et al. 2003).

Until now there has not been any study concerning the application of surfactants as pulping additives for wheat straw. Since wheat is the most abundant cultivated plant in Iran with annual grain production of about 15 MT, of which approximately 50% is lost as waste (Najafi et al. 2009), it was decided to evaluate application of beneficial surfactants in the pulping of wheat straw. Provinces that produce large quantities of wheat in Iran are Fars, Lorestan, Ilam, Khuzestan, Markazi, Hamedan, Kordestan, Zanjan, Azarbayjan, Gilan, Mazandaran, Tehran, and Charmahal (Najafi et al. 2009). Soda pulping is traditionally the most employed chemical pulping process for various non-wood raw materials, including wheat straw (Khristova et al. 2006; Enayati et al. 2009). Non-wood pulping is important especially in Iran and some other countries that don't have enough wood resources to support the pulp and paper industries.

Recent studies have shown effects of surfactants on pulping outcomes. Baptista et al. (2004) considered some surfactants from four different groups in pulping and bleaching of *Pinus pinaster* and stated that nonionic surfactants gave the best results. They observed that the value of kappa number, chemical consumption, and screen rejects were decreased, while brightness was increased. Blomstedt and Vuorinen (2007) observed that the addition of carboxymethylcellulose (CMC) and dodecyltrimethyl ammonium bromide considerably increased the internal and tensile strengths. Dugiralla (2000) observed that the addition of 0.1% surfactant to kraft pulping liquor (on oven dry wood) resulted in a more uniform cook with a significant decrease in kappa number; moreover it led to an increase of about 0.5 to 1% in the yield value at a constant kappa number. Ehara et al. (2000) used some nonionic surfactants in kraft pulping liquor, with bleaching by peroxide manganese, and they observed that the brightness value of pulps increased. Guo et al. (2002) indicated that the use of PEG in hardwood kraft pulping improved the delignification rate, selectivity, and yield value. Hamzeh et al. (2009) used some surfactants in soda pulping of baggase. Some of them improved the pulp yield, and others reduced it. All of them increased the yield of unbleached pulps and decreased the alkaline consumption and screen reject value. Mishra et al. (2007) used some non-ionic surfactants in the pulping of a bamboo and hardwood mixture. This approach resulted in reduction of extractives, kappa number, COD, TSS, and screen reject. In addition, the brightness of the unbleached pulps improved. Santiago et al. (2007) showed that the application of an alcoholic surface-active material in pulping of eucalyptus globules improved the pulp viscosity in a constant kappa number without any effect in pulp yield in comparison with conventional pulp.

EXPERIMENTAL

Wheat straw samples were obtained from wheat farms of Golestan province in Iran and they were then transported to the pulp and paper laboratory of Gorgan University. The clusters were removed, and the rest of the stalk was cut to 2-2.5 cm fragments. After being well air-dried, their moisture contents were measured. The straws were pulped in a set of six cylindrical digesters (2.5 L each) rotating in a heated glycerin bath.

Conventional cooks were carried out with the following conditions. Constant factors were: straw weight: 100 gram (based on oven dry), liquor to straw ratio 7:1, and maximum temperature, 160 °C. Variable factors were: active alkali (as NaOH) of 15, 18, and 20% on oven dry of straw and times at maximum temperature of 30, 60, 90, 120 and 150 minutes. These conditions were applied in an effort to achieve a kappa number less than 20 (bleachable pulp). The kappa numbers were measured according to TAPPI Method T 236 om-85. Under the favorable conditions that were achieved, main cooks were carried out by adding the surfactants to the cooking liquor. Surfactants were used at

0.5 and 1% dosage based on oven-dry straw. Two representative nonionic surfactants were used: lauryl alcohol ethoxylated with 7 moles of ethylene oxide per mole of alcohol (ELA-7) and poly ethylene glycol 1500 (PEG 1500). These chemicals were prepared by Iranian Kimiagaran Emrooz Co. After cooking, pulps were fully washed by water on a 20 mesh screen and collected on a 200 mesh screen. Accept yield and rejects were determined. Accepted pulps were disintegrated at 6000 rpm and then were refined to 350±25 mL CSF freeness according to TAPPI T 248 sp-00.

The control pulp and selected pulp samples with different surfactants were then bleached in a five-stage AD_0EPD_1P sequence. The A (acidic) stage was done with acidic water at a pH of 1.5 at 50°C for 30 min. The D_0 stage was performed at 70°C for 60 min. The ClO_2 charge in the D_0 stage was 3.24%. The peroxide reinforced alkaline stage was done at 70°C for 60 minutes with 1.2% NaOH charge and 0.5% H_2O_2. The temperature in the D_1 stage (ClO_2 bleaching stage) was 80°C for 80 minutes. The ClO_2 charge in the D_1 stage was 0.81%. The P stage was performed with 0.75% NaOH charge. The consistency of all pulp samples was 10% in all stages of the bleaching sequence. Standard handsheets (60 g/m2) were made according to T205 om-88 from both unbleached and bleached pulps. Strength such as tensile, tear, and burst indexes and physical properties such as density, caliper and air resistance were measured according to TAPPI standard methods. The effects of using surfactants on pulp properties were analyzed by using one way Anova, and the means were compared by using Duncan's multiple comparison test at 95% confidence level.

RESULTS AND DISCUSSIONS

Reference cooks were carried out without surfactant, and the relationships among kappa number, yield, and cooking times are shown in Table 1.

Table 1. Results of Control Cooks (Yields and Kappa No.)

AA(%) (as NaOH)	Time at maximum temperature(min)	Pulp Yield(%)		Kappa No.
		Accept	Reject	
15	90	43.6	0.94	33.8
	120	43.0	1.13	34.0
18	60	41.5	0.43	27.6
	90	39.3	0.47	21.1
	120	44.6	0.47	23.9
	150	44.1	0.58	22.9
20	30	43.3	0.60	20.7
	60	44.0	0.57	19.9
	90	42.5	0.41	18.7
	120	43.3	0.30	18.0
	150	42.3	0.30	18.2

As seen in Table 1, bleachable pulps with kappa number less than 20 could be produced at 20% AA on OD straw. The effects of using two different types of surfactants on soda pulping of wheat straw, based on optimum pulping conditions of reference cooks, are shown in Table 2.

Table 2. Results of Using Surfactants on Soda Pulping of Wheat Straw

Time at maximum temprature (min)	Surfactant dosages (%)	Kappa number		Screened yield (%)		Screen rejects(%)	
		ELA-7	PEG 1500	ELA-7	PEG 1500	ELA-7	PEG 1500
90	0	18.7		42.5		0.41	
	0.5	19	18.2	43.6	45	0.02	0.09
	1	20	20.5	43	44.7	0.01	0.0.3
120	0	18		43.3		0.3	
	0.5	19.5	21.1	42.8	45.1	0.00	0.00
	1	18	21.1	42	44.2	0.01	0.00
150	0	18.2		42.3		0.3	
	0.5	18.7	19	43.6	45.3	0.00	0.00
	1	18	18.8	43.4	44.4	0.00	0.00

Table 2 indicates that both surfactants caused an increase in the accepted pulp and decreases in reject levels. Increases in accepted pulp yield and decreased rejects were much more significant in the case of PEG 1500 than ELA-7 at comparable kappa number. In addition, the results indicated that for both surfactants, 0.5% dosage rate and 90 minutes pulping time at maximum temperature were optimum conditions for making bleachable soda pulp from wheat straw.

The increase in pulp yield at similar kappa number may be due to higher selectivity of delignification (lower dissolution of carbohydrates at certain amount of lignin dissolution), which was affected by surfactant that can act as a co-solvent (Dugiralla. 1999; Guo et al. 2003; Baptista et al. 2006; Hamze et al. 2009). According to Chen (1994) a yield increase provides economic benefits to the pulp mills. Addition of the digester additives also allows more efficient utilization of resources. It has an importance especially in some countries like Iran that don’t have enough lignocellulosic resources from forests to satisfy the needs of pulp mills.

Table 3 shows the optical and strength properties of reference pulp versus surfactant-aided pulps.

As indicated in Table 3, comparable strength and optical properties to control samples were achieved when using 0.5% ELA-7 type surfactant. However, when PEG 1500 was used as surfactant, fiber bonding related strength such as burst and tensile were decreased at comparable tear strength. By using this surfactant, optical properties were slightly improved as is indicated by higher brightness and L; but at lower a and similar level of opacity.

Surfactants can act as debonding agent, and the debonding of fibers causes an increase pore size (Shepherd and Xiao. 1999). However, for some unknown reasons, even though the fiber bonding strengths were reduced by using PEG 1500, high porosity was observed as compared to ELA-7 or the control sample.

Table 3. Physical, Optical, and Strength Properties of Unbleached Wheat Straw Soda Pulps

Properties		Brown stock pulp		
		Control	ELA-7	PEG 1500
Physical	Caliper (µm)	95.76 [a]	99.08 [a]	97.70 [a]
	Density (g/cm^3)	0.66 [a]	0.65 [a]	0.61 [b]
	Air resistance (S)	29.9 [a]	35.4 [a]	40.9 [a]
Strength	Burst Index (kPa.m^2/g)	5.68 [a]	5.93 [a]	4.99 [b]
	Tensile Index (Nm/g)	80.42 [a]	72.40 [a]	67.31 [b]
	Tear Index (mN.m^2/g)	6.6 [b]	6.6 [b]	7.2 [a]
Optical	Brightness (%)	31.3 [b]	31.2 [b]	33.1 [a]
	Opacity (%)	39.8 [b]	40.4 [a]	39.2 [c]
	L	72 [b]	72 [b]	73.5 [a]
	a	3.6 [b]	3.8 [a]	3.4 [b]
	b	16.3 [b]	16.6 [a]	16.5 [b]

Values in a row with same letters aren't significantly different at 95% confidence level.

Bleaching

The influence of using surfactants in the pulping stage on pulp bleachability was investigated in $AD_0E_PD_1P$ bleaching sequences (Fig 1). As can be seen, the bleachability of pulps was improved by using surfactants during cooking, and both surfactant-treated samples exhibited higher brightness the control samples. This may be attributed to the higher initial brightness of unbleached pulps and/or from lignin redeposition (Baptista et al. 2006; Hamzeh et al. 2009).

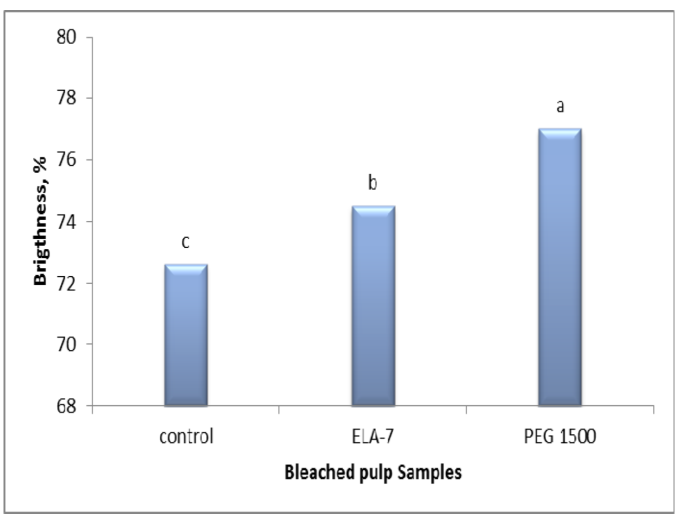

Fig. 1. The effects of surfactants on unbleached and bleached pulp brightness (Unlike letters in the figure shows significantly different at 95% confidence level).

The differences between opacity of unbleached pulps were negligible (Fig 2); also the opacity values of bleached pulps were approximately the same.

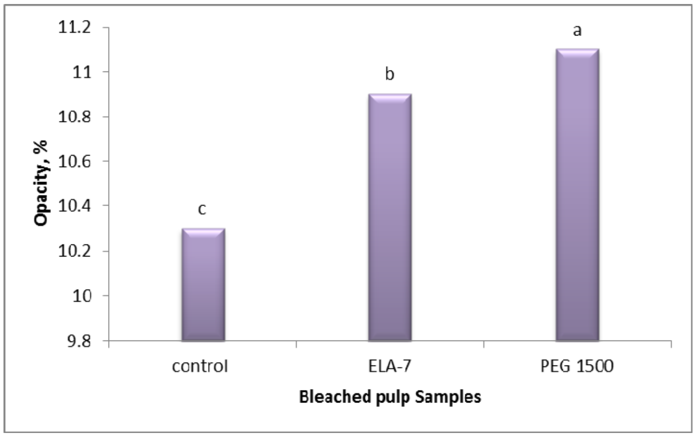

Fig. 2. The effects of surfactants on unbleached and bleached pulp opacity (Unlike letters in the figure shows significantly different at %95 confidence level).

The results indicated that application of surfactants had a favorable effect on the opacity of the pulps.

Strength Properties

Table 4 shows the physical and strength properties of bleached pulp samples.

Table 4. Strength Properties and Density of Bleached Samples

Properties		Bleached pulps ($AD_1E_PD_2P$)		
		Control	ELA-7	PEG 1500
Strength	Burst index(kPa.m^2/g)	6.14 ^{a}	6.07 ^{a}	5.23 ^{b}
	Tensile index (Nm/g)	87.20 ^{a}	86.90 ^{a}	81.17 ^{b}
	Tear index (mN.m2/g)	6.6 ^{b}	6.6 ^{b}	6.8 ^{a}
Physical	Air resistance(s)	84.5 ^{a}	45.3 ^{b}	34.6 ^{b}
	Density (g/cm^3)	0.66 ^{a}	0.68 ^{a}	0.64 ^{b}
	Caliper (µm)	97.12 ^{b}	94.26 ^{b}	100.31 ^{a}

The application of the two surfactants had similar effects on strength properties of bleached samples in comparison to the control (Table 4). The use of ELA-7 during cooking had negligible effects on strength properties, but in case of PEG 1500, the fiber-fiber bonding strength was decreased and tear strength was increased. In addition, use of the surfactant decreased air resistance value especially in the case of PEG 1500 addition for bleached pulp samples; this finding can be attributed to a debonding effect of the used surface active materials. In fact, debonding of fibers caused the resulting sheet to be more porous and bulkier. An increase in caliper and a decrease in density value confirm these results, too.

CONCLUSIONS

1. Addition of the surfactant ELA-7 didn’t significantly affect paper properties. But application of this surfactant was judged to be worthy of consideration for application in pulp mills, because it significantly improved the yield value and decreased the rejects.
2. Addition of PEG 1500 had different effects on paper properties. It improved tear strength, but it decreased burst and tensile strengths. In addition, this surfactant improved the yield and decreased the rejects even relative to ELA-7.
3. Surfactants can be recommended for pulping of wheat straw. In fact, addition of the digester additives allows more efficient utilization of lignocellulosic resources, which can be attributed to an increase in pulp yield. It has an importance especially in some countries such as Iran that don’t have enough wood resources to satisfy the needs of pulp mills.
4. Surfactant treatment improved the pulp brightness, and less bleaching chemicals were required to get the same level of brightness. Such results could be beneficial from the environmental and economic points of view.
5. The two surfactants used in this study had different effects on pulp properties. These differences were consistent with the different HLB values and different hydrophobic character of the surfactants.

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