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Effect of Urea Addition on Soda Pulping of Oak Wood

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Many studies have been conducted to find a sulfur–free additive for alkaline pulping liquors that would have an effect similar to that of sulfide in kraft pulping. Some reagents that partially fulfill this role have been found, but they are too expensive to be used in the quantities required to make them effective. As an alternative method to solve air pollution problem and difficulty of pulp bleaching of kraft pulping process, NaOH–Urea pulping was applied. The properties of NaOH–Urea pulp were compared to those of NaOH and kraft pulps. Addition of urea in low alkali charges retarded delignification rate compared to NaOH pulping. But, in high alkali application, delignification was significantly enhanced not from the addition of urea but from the high alkalinity. It was disclosed that urea did not participate on delignification reaction by the experiment using lignin model compound. Compared to paper strengths at the same level of sheet density, NaOH–Urea pulp gave as almost same breaking length and tensile index as those of kraft pulp. Especially tensile energy absorption and burst index were higher than those of kraft pulp. It is believed that, during pulping, the formation of cellulose carbamate would play a main role to enchance the paper strength.

INTRODUCTION

The problems arising from the release of sulfur compounds during kraft pulping and recovery have led to the investigation of sulfur–free pulping methods as possible alternatives. Many approaches have been considered, including the alkali process, the application of oxygen to the delignification process (Abrahamson and Samuelson, 1979; Aoyagi *et al*., 1977; Worster and Pudek, 1974) , and the use of organic additives (Abbot and Bolker, 1982; Daima *et al*., 1978; Nakano *et al*., 1976; April *et al*., 1982; Sakakibara, 1983) to perform a role similar to that of sulfide in the kraft process. These additives may be used to allow complete removal of sulfide from the system or to reduce the sulfidity level during digestion to a point where odor from the black liquor system is more readily controlled. Many studies (Kalish, 1967; Huynh *et al*., 1982; Cho, 1983; Worster and Pudek, 1974a; 1974b) have been conducted to find a sulfur–free additive for alkaline pulping liquors that would have an effect similar to that of sulfide in kraft pulping. Some reagents that partially fulfill this roll have been found, but they are too expensive to be used in the quantities required to make them effective.

One type of reagent, namely anthraquinones and compounds of a related structure (Flemming *et al*., 1978; Ghosh *et al*., 1978; Holton and Chapman, 1977; Obst, 1979; Yaguchi, 1979), has been found to have a marked effect on kraft and alkali pulping, even in very small quantities. Although some research works on NaOH–Urea pulping (Tripath and Basu, 1967; Draganova *et al*., 1971; Lyubavskaya and Voronova, 1977; Popescu and Nita, 1983) have been done, most of them were mainly about the effect of urea additive on delignification, there were few papers on the sheet properties of NaOH–Urea pulp. This study was performed to find out the effect of urea addition to NaOH cooking liquor on the pulping of oak wood and its pulp properties.

EXPERIMENTAL

Pulp preparation

Oak wood chips were cooked in a 5 l. capacity stainless steel digester, using liquor to wood ratio, 8:1, time to maximum temperature, 90 min., at maximum temperature of 170 °C for the certain cooking times. Charges of 350 g (O.D.) chips were used for the NaOH and NaOH–Urea cooks, with active alkali of 18%. Charges of urea in alkali cooking media were 4 and 8% based on wood chip. Kraft pulp was prepared by cooking 350 g chips using a 18% active alkali and sulfidity of 25%. Cooked chips were disintegrated, thoroughly washed, dewatered to a moisture content of ca. 90%, crumbed in plastic bags without screening and stored in refriegerator for the next processing. In order to confirm the effect of urea addition during NaOH cooking on delignification, lignin model compound, guaiacylglycerol–β–guaiacyl ether (GG ether), was synthesized by Hosoya's method (Hosoya and Nakano, 1980) and subjected to NaOH and NaOH–Urea cooks. Degradation product from GG ether was determined by G.L.C.

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Pulp evaluation

Pulps were beaten in a PFI mill with a 30 g (O.D.) charge at 10% stock consistency using a beating load of 3.4 kg/cm and a relative speed of 6 m/s. Handsheets (*ca.* 60 g/m^2 O.D. Grammage) were prepared from 3 different freeness level pulps according to Korean Standard. Handsheets were tested according to Korean Standard methods after conditioning in an atmosphere of 50±2% of relative humidity at 23±1 °C. Water retention values of pulps also were determined by the procedure using centrifugal forces of 3000 G for 15 min.

RESULTS AND DISCUSSION

Pulping

The variation in pulping results was shown in Table 1. The NaOH cooking was reasonable in terms of pulp yield and delignification rates compared to the NaOH–Urea cooking. Though, at the same cooking time, NaOH pulping was shown high delignification rates, net yields subtracted lignin fraction were lower than those of NaOH–Urea.

The addition of 4% urea produced a higher pulp yield than that of NaOH for the almost same degree of delignification. And the increase in urea addition, especially such as 8%, resulted the pulp with an unacceptably high residual lignin. The optimum pulping conditions were 90 min. cooking at 170 °C using 4% urea in 18% active alkali.

Table 1. Cooking of oak wood with NaOH–Urea

Cooking chemical	Cooking time min	Pulp yield %	Klason lignin %	Delignification %
NaOH	90	51.7	3.77	91.8
	120	50.2	5.27	88.9
	150	51.9	6.75	85.3
NaOH+ 4% Urea	90	54.2	4.38	90.0
	120	59.1	7.41	81.6
	150	59.3	8.87	77.9
NaOH+ 8% Urea	90	71.0	12.5	62.7
	120	70.0	11.1	67.4
	150	69.5	11.8	65.6

Effect of urea addition

As shown in Table 2, it was observed that addition of urea in low alkali charges, such as 0.5 N, retarded delignification rate compared to NaOH pulping.

But, in high alkali application such as 1 N NaOH, delignification was significantly enhanced. It was believed that these results were attributed to not the addition of urea but the high alkalinity. In addition, the changes in final pH of cooking liquor were big enough to disturb the delignification by addition of urea. Namely urea consumed much alkali during cooking as shown in Table 2. Though there were no changes in final pH of cooking liquor in the case of 1 N NaOH application, final pH was abruptly reduced for the NaOH–Urea cooking in low alkali charge such as 0.5 N NaOH.

In order to know what component in wood consume the alkali, wood chip, woodmeal, organosolve lignin and avicel were treated with NaOH and NaOH–Urea as shown in Table 3. In the case of NaOH only there were no changes in pH except woodmeal.

By adding urea in NaOH, it was noticeable that there were a great decreasing in final pH, especially in woods and avicel. It meant that the urea did not react with lignin fraction, but played a role to have react with carbohydrates, mainly cellulose, and have them consume the alkali.

Reaction of urea with cellulose in an aqueous medium at different temperatures has been widely studied by many researchers for the modification of cellulosic textile finishing (Hebeishi *et al.*, 1978; Nozawa and Higashide, 1981) and the improving mechanical properties of paper (Fisher, 1951). While at 100 °C hydrogen bonds between urea and cellulose hydroxyls took place, at 150 °C the system was very complex, since crosslinking of cellulose, cellulose derivateves of urea, dimerization, as well as decomposition of urea could be realized. It was also reported that urea reacted with alcohols and polyhydric alcohols to bring about the corresponding carbamate esters (Jacobson, 1938; Nuessssle, 1961; Segal and Eggerton, 1961). There would be some possibility that carbamates and cellulose carbamates derived during cooking consumed the alkali. It was not known why woodmeal consumed so much chemicals in the presence of urea compared to the wood chips.

Table 2. Effect of Urea on final pH of cooking liquor during NaOH cooking (170 ℃, 90 min.)

Cooking	Yield, %	Kraft lignin %	Final pH
0.5N NaOH	55.5	3.62	14.0
0.5N NaOH +4% Urea	62.8	11.9	13.3
1.0N NaOH	47.9	2.89	14.0
1.0N NaOH +4% Urea	49.3	3.81	14.0

Table 3. Changes in pH of cooking liquor after NaOH–Urea cooking

Sample	NaOH	NaOH + Urea
Wood chip	14.0	13.3
Woodmeal	13.5	12.7
Organolignin	14.0	14.0
Avicel	14.0	13.5

Table 4. Relative yields of guaiacol from guaiacylglycerol–β–guaiacyl ether (GG) by NaOH and NaOH–Urea cooking

Cooking liquor		Relative yields of Guaiacol, %
NaOH	Urea, %	
1 N	0	100
1 N	1	95.3
1 N	2	98.5
1 N	3	98.0

In order to confirm the effect of urea addition during NaOH cooking on delignification, lignin model compound, guaiacylglycerol–β–guaiacyl ether (GG ether), was subjected to NaOH and NaOH–Urea cooks. The yields of degradation product, guaiacol, from GG ether were as same as those by NaOH cooking as in Table 4. Therefore it was evident that urea did not participate on delignification reaction.

Pulp properties

Table 5 gave the pulping features compared with a kraft reference pulp. For the same degree of delignification, the yield of NaOH–Urea pulp was same or/and to some extent higher than the others. It is believed that higher yield of formers may attributed to the blocking effect of its peeling off reaction by some modification of reducing end groups of carbohydrates with the formation of cellulose carbamate ester. NaOH–Urea pulp had higher brightness than that of kraft.

Table 5. Pulping characteristics of oak wood with NaOH–Urea

Properties	NaOH	NaOH + 4% Urea	Kraft
Pulp yield, %	51.7	54.2	53.7
Klason Lignin, %	3.77	4.38	4.05
Brightness (Hunter), %	29	26	20

Figure 1 showed the revolution numbers of PFI mill for the pulps. NaOH–Urea pulp was more difficult to beaten than kraft pulp, but relatively easier than NaOH pulp. In order to get 450 ml freeness, the revolution numbers for kraft pulp was 1,230×10^2, NaOH–Urea pulp 1,450×10^2, and NaOH pulp 1,600×10^2. The resistance of pulp refining are closely related to the flexibility of pulp fibers. Kraft pulp had highest water retention value of 489. Those of NaOH–Urea and NaOH pulps were 434 and 338, respectively.

Table 6. Physical and mechanical properties of NaOH–Urea pulp

Properties	NaOH	NaOH + 4% Urea	Kraft
Freeness, CSF ml	380	400	360
Sheet Density, g/cm^3	0.71	0.75	0.85
Breaking length, km	6.98	8.44	9.71
Tensile index, N.m/g	68.4	82.8	95.2
Tensile energy absorption, J/m^2	123	202	192
Burst index, kPa.m^2/g	4.67	6.19	6.47
Tear index, mN.m^2/g	4.54	8.80	6.92
W R.V, %	338	434	489

Table 6 was shown papermaking properties of various pulps. The hand sheet strength properties of NaOH pulp were slightly lower than for the other two pulps. When compared at both the same freeness level, NaOH–Urea pulp had slightly lower tensile and burst strengths than kraft pulp, whilst tensile energy absorption and tear index were considerably increased. Apparent ssheet density of kraft pulp were higher than NaOH and NaOH–Urea pulps at the same level of freeness.

Breaking length failure will occur as the result of inadquate bonding or fiber failure. The latters becomes more significant as bonded area increases with a simultaneous increase in sheet density and tensile strength. As can be seen Fig. 2, there was a linear relationship between breaking length and sheet density. The slope of breaking length is affected by bonding strength. Those of NaOH–Urea and kraft pulp were shown almost same tendency. But NaOH pulp showed relatively inferior strength. Compared to paper strengths at the same level of sheet density, NaOH–Urea pulp gave as almost same breaking length and tensile index as those of kraft pulp. Burst strength, however, was higher than the kraft at same level of density.

Though tensile and burst indices of NaOH–Urea pulp were lower than those of kraft pulp at the same level of freeness, burst strength of the former were higher than that of kraft pulp compared at the same tensile strength as shown in Fig. 3. The kraft pulp showed lower burst at high tensile index than NaOH–Urea pulp with higher burst at low tensile index, where-

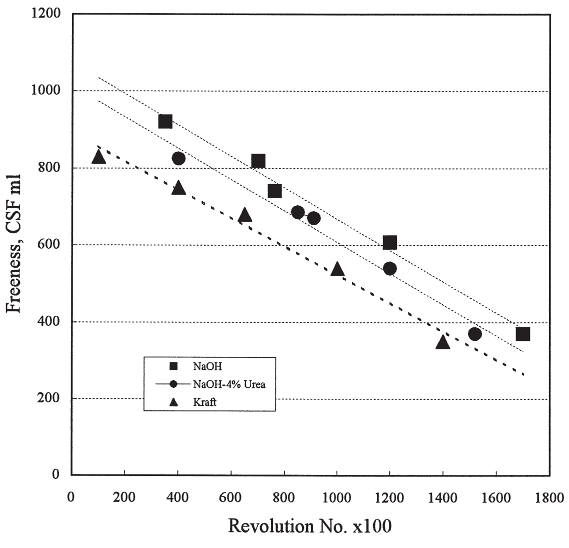

Fig. 1. Revolution number in PFI mill refining.

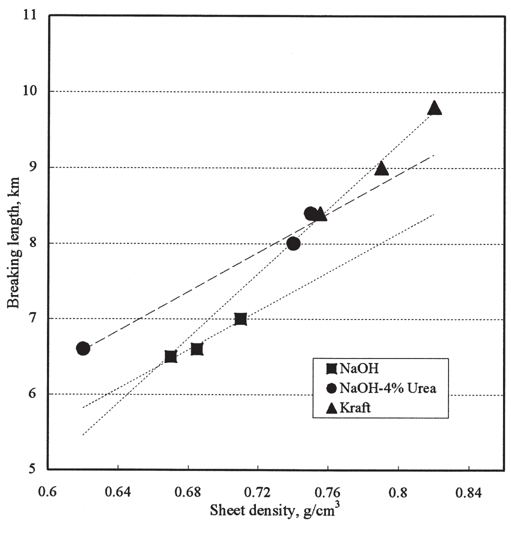

Fig. 2. Sheet density and breaking length.

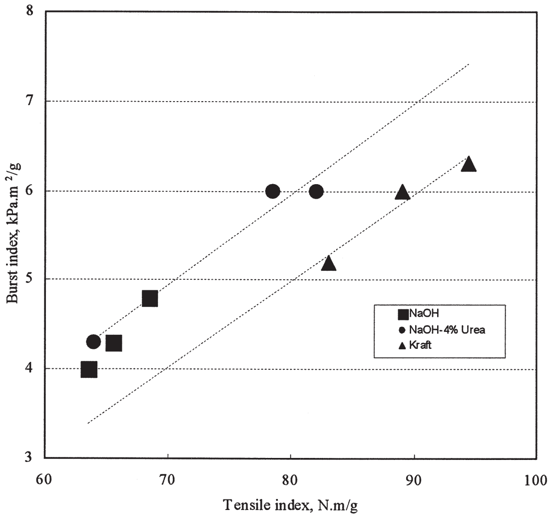

Fig. 3. Tensile index and burst index.

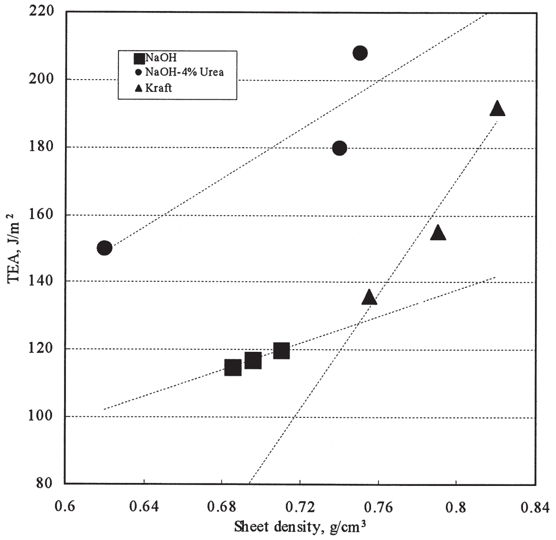

Fig. 5. Sheet density and tensile energy absorption.

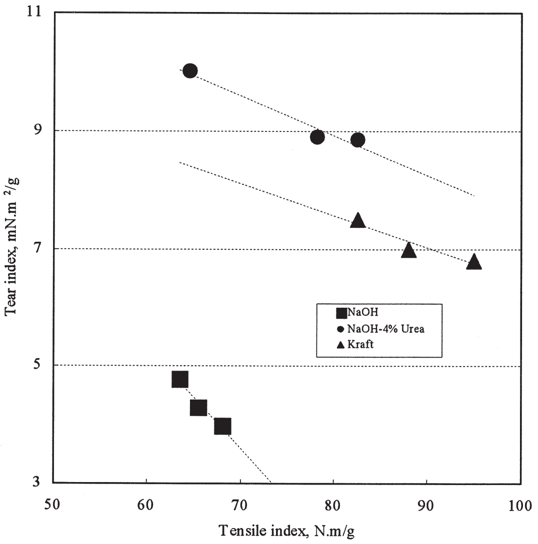

Fig. 4. Tensile index and tear index.

Table 7. Carbohydrate composition of unbleached pulps

Chemical component %	Wood	NaOH pulp	NaOH + Urea pulp	Kraft pulp
L–Arabinose	2.03	0.1	0.1	0.32
D–Xylose	22.4	7.3	7.75	8.49
D–Mannose	1.2	0.1	trace	0.3
D–Galactose	0.9	trace	trace	0.1
D–Glucose	48.5	41.6	43.8	42.3
L–Rhamnose	trace	trace	trace	trace
Lignin	23.8	1.95	2.37	2.18

as NaOH pulp showed low burst at low tensile. Three pulps have all been prepared from same wood, but the tear/tensile relationship were markedly different as shown in Fig. 4. The NaOH–Urea pulp was the highest tear index at a low tensile index than NaOH and kraft pulps. The kraft pulp gave intermediate tearing resistance at relatively high tensile index, whereas the NaOH pulp had low tear and low tensile property. The cause could be related to tensile property. The higher tensile strength of a pulp would normally indicate either a longer fiber or a higher basic density of wood. In present experiment, since all three pulps were made by same wood, the effect of fiber length, fiber length distribution and of variability in their cross dimensions on the tensile strength would be needed for more detailed knowledge.

There was a linear relationship between tensile energy absorption and sheet density. Although breaking length and tensile index of NaOH–Urea and kraft pulp were shown almost same, tensile energy absorption of the former as burst strength was much higher than that of the latters. But NaOH pulp showed relatively low strength. Compared to the strength at the same level of sheet density, NaOH–Urea pulp were shown very high tensile energy absoprtion as in Fig. 5.

Table 7 showed the carbohydrate compositions of different pulps compared with those of the original wood. For the kraft pulp hemicellulose contents were higher than for the NaOH and NaOH–Urea pulps. In the case of NaOH–Urea pulp glucan contents were higher than the others. These results would be contributed to the increase of pulp strength compared to that of NaOH pulp.

CONCLUSIONS

As an alternative method of kraft pulping process, NaOH pulping used cheap urea additive was adopted. The results were compared to the properties of NaOH and kraft pulps, and summarized as follows. NaOH–Urea cooking in low alkali charges, regardless of added amounts of urea, gave a relatively low delignification rate compared to NaOH pulping. But, in high alkali application, the delignification of oak wood was significantly enhanced. In the lignin model compound experiment, it was disclosed that urea did not participate on delignification reaction. The optimum condition was 90 min. cooking at 170 °C using 4% urea in 18% active alkali. Beatability of NaOH–Urea pulp was a little faster than NaOH pulp, but slower than kraft pulp. Pulp brightness was a little higher than kraft pulp. Compared to sheet strengths at the same level of sheet density, NaOH–Urea pulp gave as almost same breaking length and tensile index as those of kraft pulp. Especially tensile energy absorption and burst index were higher than those of kraft pulp. Every property was superior than those of NaOH pulp.

This pulping method would appear to be one of the promising approach because the small amounts of urea in aqueous alkaline medium have the ability to stabilize carbohydrates against their peeling off reaction. Also, it is believed that, during pulping, the formation of cellulose carbamate would play a main role to enchance the paper strength.

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