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Deinking of Electrostatic Wastepaper with Cellulolytic Enzymes and Surfactant in Neutral pH

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ABSTRACT

Enzymatic deinking method can avoids the alkaline environment as usual required in chemical deinking, which consequently cuts chemical costs and reduced the white water pollution. The electrostatic wastepaper was dinked with commercial cellulolytic enzymes and surfactant in neutral pH and the effectiveness of deinking and the physical properties of deinked pulp were evaluated. The disintegrating efficiency of the electrostatic wastepaper in neutral pH was enhanced with enzyme treatments. Although the freeness of deinked pulp with enzymes was higher than that of deinked pulp with chemical deinking agents, the brightness of the enzymatic deinked pulp was slightly lower than that of the chemical deinked pulp. But, by additions of nonionic surfactants, the brightness of deinked pulp was increased with less residual ink particles and mechanical properties of enzymatic deinked pulp was improved compared to the deinked pulp of conventional alkaline method.

Keywords : *deinking, commercial cellulolytic enzymes, neutral pH, surfactant*

1. Introduction

Wastepaper is one of the major resources for the paper industry that is being oriented towards re-use and sustainability. To facilitate the use of paper made with wastepaper, wastepaper-based products must compete with virgin equivalent and must perform well during conversion and meet the same end- product specifications.

However, there has been a substantial increase of wastepaper such as CPO (computer print out), W/L (white lager) and MOW (mixed office waste) from xerographic and laser- printed papers which are refer to difficult to be deinked. Since the waste paper was composed of high grade of bleached chemical pulp, it can be used in a high grade of paper manufacture if contaminants were removed efficiently from the pulp (1).

The paper recycling process have a deinking operation for removal of ink particles prior to waste paper recycling. Deinking is necessary to achieve minimum brightness values required for printing and writing grade papers. The conventional deinking

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method should need much of chemical agents, such as sodium hydroxide, sodium carbonate, hydrogen peroxide and surfactants (2, 3).

However, there has been a substantial increase in the portion of difficult-to-deink with the conventional deinking method xerographic or laser printed papers in recovered waste papers. The toner ink of xerographic or laser printer is composed mainly of carbon black as pigment and polystyrene and /or polyacrylate as binders which are hardened with heat (70-120℃) during the printing process. Nevertheless, the thermoplastic polymer is attached to paper so strongly that it is difficult to detach from fiber with conventional deinking method of that kind of waste papers. Even though the toner ink was detached from pulp, it has too big plat size to reject with screen or cleaner (4, 5). Also, it is difficult to reject with an alkaline soap flotation method because a hairy particle (mixture of toner ink and fiber) is hydrophilic.

It must be need therefore much more dosage of chemical agents such as sodium hydroxide et al for deinking of the xerographic and laser- printed papers comparing of normal ink printed waste paper, resulting in a costly wastewater treatment to meet the environmental regulations (6).

Many approaches have been suggested to solve the problems encountered by traditional deinking techniques (7, 8).

Biodeinking is proposed as an alternative since it was known that enzymatic deinking is beneficial to decrease the usages of chemicals and water compared to conventional alkaline methods (9). The magnetic deinking method has shown potential for separation of toner particles from fibers based on magnetic contained in toners from laser printers and copiers. The combined technology of enzymatic and magnetic deinking was compared to the conventional enzyme/ flotation process (10).

More recently, alkaline actives cellulolytic enzymes were used for deinking of waste papers (11-13). Neutral deinking methods have also been reported. Neutral deinking performed at neutral pH of all process water. In contrast to a conventional deinking at high pH, neutral deinking method can avoids the alkaline contaminants and a yellowing of pulps. Much less amount of chemical agents are therefore need for bleaching of deinked pulp. However, the ink particles removal efficiency of this method might be less than that of the conventional alkaline deinking method. Since the enzymatic activities can promote detachment of ink and dirt from electrostatic waste paper, enzymatic deinking with surfactant should be promised method in neutral pH process.

In this paper, the mixed office wastepaper (mainly, electrostatic wastepaper) was deinked with commercial cellulolytic enzymes and surfactant in neutral pH, deinking effects were evaluated by brightness, residual ink and dirt counts of handsheets made from the deinked pulp. Also, the physical properties of deinked pulp were compared to that of alkaline deinking method.

2. Materials and Methods

2.1 Materials

The electrostatic wastepaper used in this experiment was a mixture of photocopier papers, so-call MOW (mixed office wastepaper) that were coated with toner and laser print- outs. MOW was torn into small pieces by hand and keep in vinyl pack. Denimax BT (Novo. Co.)was used for enzymatic treatment. The optimal pH and temperature of Denimax BT treatment are 6-8 and 45-60℃. Anionic surfactant (DI-100, Shinyong Co., Korea) was used for enzymatic and alkaline deinking methods.

2.2 Methods

2.2.1 Disintegration of MOW

40 g of MOW was adjusted 4% consistency with a 55℃, pH 7.0 of tap water which contained enzymes (0.1% based on dried MOW). After 10 min. of soaking,

the MOW was disintegrated in a Canadian standard laboratory pulper. The pulper revolution was controlled from 1000 to 5000. The fiber bundles which were unfibrilated in the pulper were removed with Sweco screen and measured its dry weight. Heat killed (70℃, 2 hr) enzymes and alkaline condition (pH 10.5) with 0.1% NaOH were used as controls for comparing of enzymatic effect of paper disintegration.

2.2.2 Deinking of MOW

MOW was pulped with only 0.4% of enzymes and with enzymes and 0.3% of synthetic anionic surfactant and with 1.5% NaOH and 0.3% of synthetic anionic surfactant to compared. The pulp slurry of MOW (conc. 1%) was deinked with 3 L of laboratory flotation cell (Voith 2-18) for 5min. at 50℃ with an air flow of 3 L/min. Deinked pulp was dewatered and keeped in refrigerator. Handsheets of deinked pulp were made with a standard TAPPI handsheet mold according to TAPPI method T205. The pad for brightness determine were prepared by TAPPI method T218. The brightness of deinked pulp was determined by TAPPI method T452.

2.2.3 Image analysis

For microscopic analysis of ink particle, deinked pulp was diluted to a consistency of 0.01% and filtered with cellulose acetate filter (Sartorius Ltd., 0.8 micrometer). About 10 mg of dispersed ink particle and fiber mixture was collected from 100 ml of diluted pulp suspension. Three slide glasses of cellulose acetate filters were made for microscopy. The slide glasses were take a photograph at 10 randomly selected areas (2×2 cm^2) with an optical microscopy equipped with a camera. The photograph was scanned by a photoscanner with an optical resolution of 1200 dpi. The scanned data was analyzed with an image analyzer (JX-330).

2.2.4 Physical properties

The pulp freeness and the water retention value were determined by TAPPI method T227 and TAPPI um-256.

The fines content was determined with Britt's Dynamic Drainage Jar according to TAPPI method T 261.

$$F(\%) = \frac{(A \times C) - B}{A \times C} \times 100$$

F : Fines contents, %,
A : Weight of original sample, g
B : Weight of fiber pad, od., g,
C : Consistency, g/g

The distribution of fiber length was determined with Kajaani FS-200. The physical properties of handsheets were determined according to the TAPPI method T404 (tensile strength) and TAPPI method T 403 (burst strength).

3. Results and Discussion

3. 1 The disintegrating efficiency of MOW with emzyme

Amount of Sweco screen passed fibers from pulped slurry of MOW is most high at alkaline pulping within 2000 revolution of Canadian standard laboratory

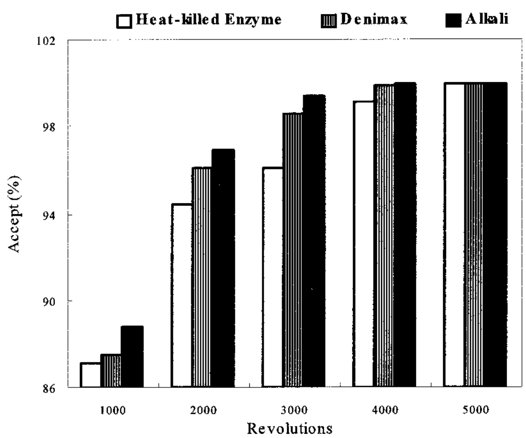

Fig. 1 Efficiency of disintergrating with enzymes.

Table 1. Residual ink area on DIP **(Unit : ppm)**

	Blank	Control	0.1E	0.4E	0.7E	1.0E
Area	6.3	0.3	1.5	0.9	0.7	0.7

E : enzyme dosage(%) based on dry MOW

pulper. It means that alkaline swelling is more effective to disintegrate of MOW than bioactivity of enzymes at early stage of pulping. But, as comparing of heat killed enzymes, the bioactivity of enzymes can accelerate disintegrating of MOW. After 4000 revolution of pulping, MOW was disintegrated 100% in alkaline also in enzyme condition as Fig. 1. This result means that enzyme can alternate alkali for disintegrating of paper.

3. 2 Deinking of MOW with enzyme only

The brightness of deinked pulp was increased with enzyme dosage. But, the reject content was also increased with brightness of pulp. This means that the ink removal efficiency is not improved with enzyme only.

As we can see in Table 1, residual ink area on DIP from enzyme method are more wide than control DIP which are deinked with surfactant method. But, the reject content was also increased with brightness of pulp.

3. 3 Properties of Deinked of MOW with enzyme only

The CSF and fine content of DIP was shown in Fig. 2. While the pulp freeness were increased with enzyme dosage, the fines content were decreased. This means that microfibrile which could disturb dewatering of pulp on the fiber surface and fine substance were hydrolyzed with enzyme.

Fig. 3 shows the change of water retention value of DIP on enzyme dosage. he water retention values of DIP which were treated with below 0.4% of enzyme were quite lower than blank, but the value was increased with 1% of enzyme to almost same level of blank. It can be supposed that removal of honified fibril by enzyme lead to increasing of water retention value.

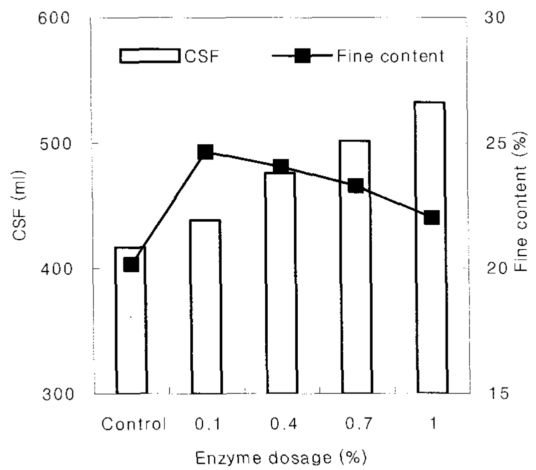

Fig. 2. The CSF and fine content of DIP on enzyme dosage.

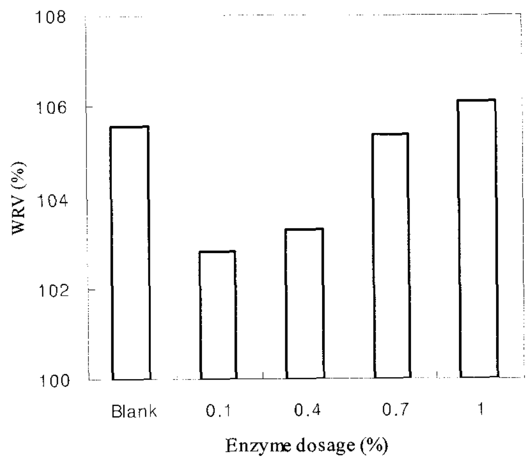

Fig. 3. The change of water retention value on enzyme dosage.

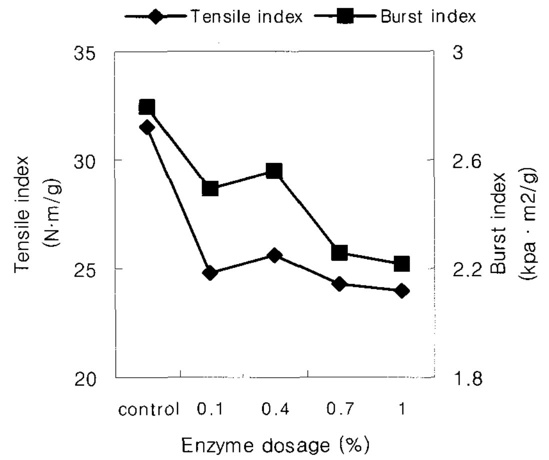

Fig.4. The mechanical properties of hand sheet of DIP deinked with enzyme only.

The mechanical properties of hand sheet of DIP with enzyme only was show in Fig. 4.

The tensile and burst strength of DIP were below than that of control. Although the enzymatic DIP has similar fiber length and even higher water retention value than control, the mechanical properties of handsheet lower than that of control. This means that inter fiber bonding was decreased with extreme remove of fiber surface microfibril.

Fig. 5 was SEM photographs of enzymatic deinked MOW pulp. As we can see from photographs, the fine and microfibril were removed with enzyme effectively. The removal of fine and microfibril might be cause decreasing of mechanical properties of handsheet. But, 0.4% of enzyme can improve the mechanical properties of handsheet temporarily. We can suppose from this result that the new hydrophilic surface was formed with enzyme.

3. 4 Deinking of MOW with enzyme and surfactant

The brightness of DIP and amount of reject from flotation with 0.4% of enzyme and surfactants were shown in Fig. 6. The brightness of DIP was increased with surfactant dosage. The surfactant might be

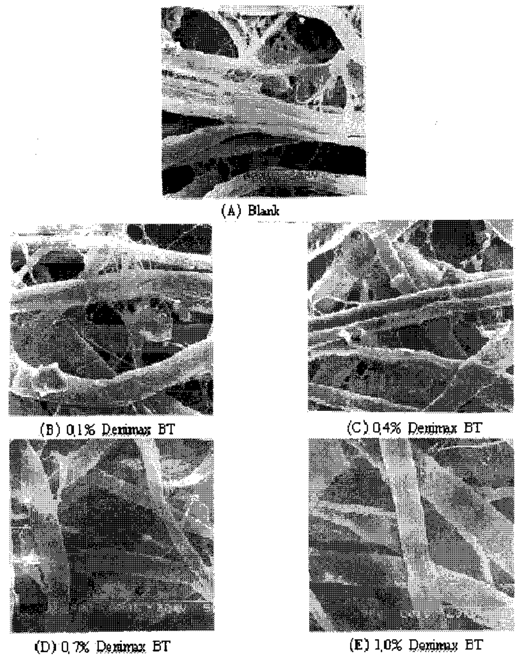

Fig. 5. SEM of enzymatic deinked pulp.

enhanced the removal of ink particles with suitable air form. Otherwise, amount of reject was decreased with surfactant dosage. Although, the higher amount of reject was obtained from flotation, the higher brightness of DIP was obtained commonly.

But, more amount of surfactant cause the high brightness and low reject amount in the enzymatic

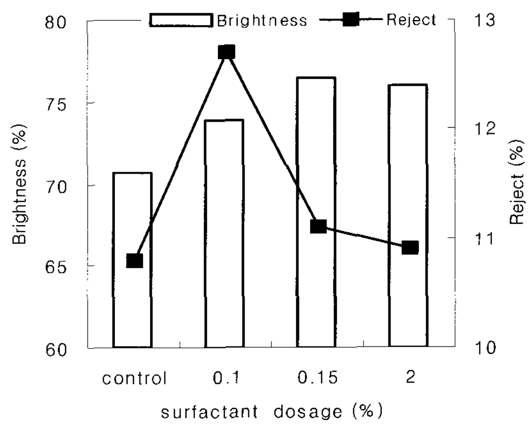

Fig. 6. The brightness and fiber yield of DIP on surfactant dosage.

Table 2. Residual ink area on DIP **(Unit : ppm)**

	Control	0.05% S	0.1% S	0.2% S
Area	0.30	0.18	0.16	0.06

S; surfactant dosage(%) based on dry MOW

deinking. It means that the size and stability of bubble is very important for deinking of MOW.

The residual ink area on the handsheet of DIP show in Table 2. The residual ink area on the handsheet of DIP decreased with 0.2% of surfactant up to 0.06 ppm, while that of control is 0.3 ppm.

Enzymatic deinking with surfactant might enhanced the deinking effect comparing to enzyme only deinking and surfactant only deinking in aspect of the residual ink area on the handsheet of DIP as well as in that of brightness. Although the ink particles were detached efficiently from fiber and dispersed by enzymatic actives, the air bubbles were too small in amount and weak to convey an adhering particles to surface of the slurry or suspension.

Therefore, small amount of the surfactant should need for enzymatic deinking of the electrostatic wastepaper such as MOW.

The distributions of residual in particle size on handsheet of DIP were shown in Fig. 7 (deinked with enzyme only) and Fig. 8 (deinked with enzyme and surfactant). As well as the result of total residual ink area on the handsheet of DIP, competively big size of ink particles were remained in handsheet of enzyme only deinked pulp. But, account of big size of ink particle were decreased with enzyme dosage in enzyme only deinking process (Fig. 7). It can be suggest that the big size ink particle was minimized and/or was removed more easily in flotation with more enzyme activity and air bubble which come from enzyme protein.

The big size of ink particle as well as more small size were removed efficiently with only small amount of surfactant (Fig. 8). The surfactant can make enough and stable air bubble for froth flotation of competitively big and rigid and hydrophobic ink particle such as electrostatic printing paper. Laser printers and photocopiers physically bind the ink

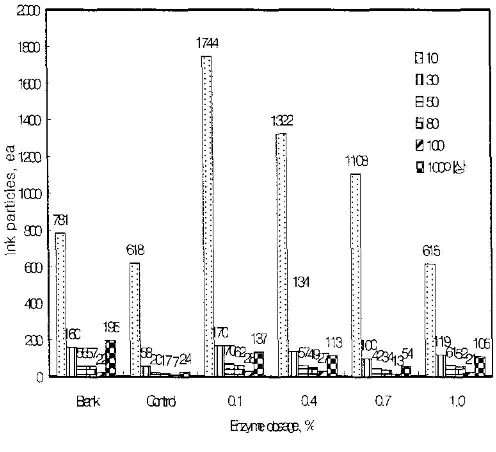

Fig. 7. The distribution of residual ink particle size on handsheet of deinked with enzyme only.

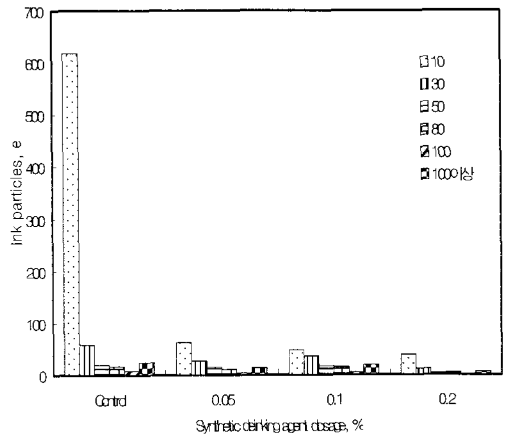

Fig. 8. The distribution of residual ink particle size on handsheet of deinked with enzyme and surfactant.

which have thermosetting toners consisting of non-dispersible synthetic polymers to the paper as a result of high heat, make it difficult to remove.

The enzyme can help releasing the those polymeric adhered ink particles from MOW. The surfactant can make the stable air bubble for froth flotation. The synergic effect of enzymes and surfactants make deinking of electrostatic paper efficiently.

Fig. 9 show the mechanical properties of deinked DIP with enzyme and surfactant. As well as enzyme only deinked DIP, the tensile and burst strength were lower than those of control. The alkaline swelling of fiber cell wall in conventional deinking method (control) can increased intra fiber bonding area in DIP from wood-free waste paper. Although enzyme treatments increased freeness and slightly decreased intrinsic fiber strength, the strength of handsheet was remained unaffected or even marginally improved. But, the mechanical strengths of DIP deinked with enzyme and 0.15% of surfactant were more strong than that of DIP deinked with enzyme and 0.1% of surfactant. This improvement of mechanical strength was may be caused by good sheet formation because the more amount of toners and laser print-outs which can disturbing good sheet formation.

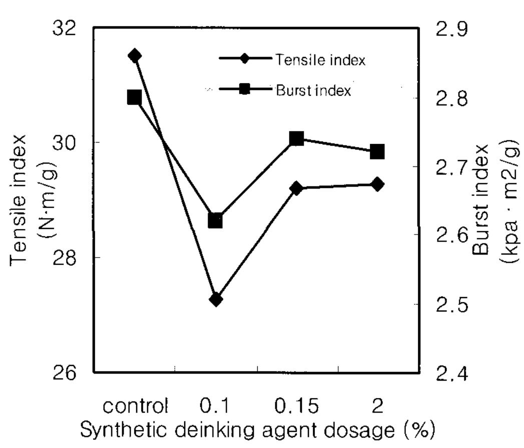

Fig. 9. The mechanical properties of handsheet.

4. Conclusions

The electrostatic wastepaper was dinked with commercial cellulolytic enzymes and surfactant in neutral pH and the effectiveness of deinking and the physical properties of deinked pulp were evaluated. The disintegrating efficiency of the electrostatic wastepaper in neutral pH was enhanced with enzyme treatments. Although the freeness of deinked pulp with enzymes was higher than that of deinked pulp with chemical deinking agents, the brightness of the enzymatic deinked pulp was slightly lower than that of the chemical deinked pulp. But, by additions of nonionic surfactants, the brightness of deinked pulp was increased with less residual ink particles and mechanical properties of enzymatic deinked pulp was improved compared to the deinked pulp of conventional alkaline method.

Literature Cited

1. Norman, J. C., Sell, Nancy, J., Daneiski, M.. Deinking laser print paper using ultrasound, Tappi J. 77(3): 151-158 (1994).
2. Eom, T.J., Micronization and deinking of laser printed ink with polysaccharides, J. of Korea Tappi 27(3): 61-67 (1995).
3. Eom, T.J., Ow, S.K., Enzymatic deinking method of old news paper, Japan Tappi 45(12): 1377-1382 (2004).
4. Dorris, G.M., Page, M., Deinking of toner printed papers, J. of Pulp and Paper Science 23(5): 206-215 (1997).
5. Bajpai, P., Bajpai, P.K., Kondo, R., Biotechnology for environmental protection in the pulp and paper industry. Springer, Berlin, Germany (1999).
6. Prasad, D.Y., Heitmann, J.A., Joyce, T.W., Enzyme deinking of colored offset print. Nor. Pulp Paper Res. J. 2: 284-286 (1993)
7. Mutje, P., Roux, J.C., Delpech, F., Carrasco, F., Flotatio deinking of recovered paper printed with laser inks, Progress in paper recycling 6(3): 48-55 (1997).

8. Qien , Y., Goodell, B., Deinking of laser printed copy paper with a mediated free radical system, Bioresource technology 96(8): 913-920 (2005).
9. Jeffries T.W., Klungness, J.H., Sykes, M.S., Rutledge, C.K.R., Comparison of enzyme enhanced with conventional deinking of xerographic and lazer printed paper. Tappi J. 77(4): 173-179 (1994).
10. Gubitz, G.M., Mansfield,S.D., Bohm,D., Sadler,J.N., Effect of endoglucanases and hemicellulases in magnetic andflotation deinking of xylographic and laser plinted papers. J. Biotecnol. 65: 209-215 (1998).
11. Pinder, K.L., Magnetic deinking of office wastepaper, Pulp and Paper Canada 97(11): 28-30 (1996).
12. Santosh,V., Anil, L., Biodeinking of mixed office waste paper by alkaline active celluloses from alkalotolerant Fusarium sp., Enzyme and Microbial Technology 32: 236-245 (2003).
13. Eom, T.J., Kang, S.H., Lee, J.M., Park, S.B., Recycling of waste paper with alkaline cellulolytic enzymes, J. Korea Tappi 36(1): 30-36 (2004).
14. Marchessault ,R.H., Debzi, E.M., Excoffer, G., Deinking of xerographic prints assisted by steam explosion, Pulp and Paper Canada 98: 59-62 (1997).
15. Elegir, G., Panizza, E., Canetti, M., Neutal enzyme assisted deinking of xerographic office waste with a cellulose/amylase mixture, Tappi J. 83: 11-17 (2000).