THE INFLUENCE OF PULP REFINING ON DE-INKING POTENTIAL AND STRENGTH PROPERTIES OF INK JET PRINTED PAPER

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The effect of laboratory refining on de-inking potential of inkjet printed handsheets was investigated. Pulp samples containing 80% short fiber and 20% long fiber were beaten in a PFI mill to reach four predetermined freeness levels of 650 (unrefined), 550, 430, and 340 mL CSF, and then handsheets were made. Handsheets were identically inkjet printed and then de-inked. Results revealed that, at lower freeness value, the brightness of de-inked pulps was higher, but the opacity decreased. The surface roughness of handsheets produced using different refined pulp before de-inking was reduced. Our results showed that refining will impart a positive effect on handsheets' de-inking potential, and de-inking printed papers produced from pulps refined to lower freeness generated the highest brightness. The results revealed that both tensile and tear strength indices of de-inked pulp were lower. However, the tear strength index of unrefined sample and the tensile strength index of pulp refined to 430 ml CSF were higher than for undeinked samples.

Keywords: Refining; De-inking; Roughness; Brightness; Opacity; Strength

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INTRODUCTION

The ever-increasing demand for paper and paper products, coupled with the shortage of wood fiber resources, has forced industry to search for alternative fiber supplies. Among various alternatives, paper recycling has been a viable solution to provide a suitable substitute for virgin fibers. Consequently, many countries, especially those that are faced with the lack of suitable fibers, have expanded paper recycling. Since the mid 1980's, the consumption of recycled paper increased, thanks to lower cost, lower energy requirement, and lower environmental impacts.

The performance and quality of recycled paper pulp to be used as the fibrous component in the manufacture of tissue and writing and printing paper primarily depends on the success of deinking process (Pathak *et al.* 2011), and the prime aim of deinking is the detachment of ink particles from the surface of the fibers using some chemicals and separating these particles from the fiber slurry. Both phenomena are influenced by the kind of ink used in the printing process and the physical chemistry and topography of the paper surface (Thompson 1998; Lane *et al.* 2010; Lee *et al.* 2011; Xu *et al.* 2005; Moutinho *et al.* 2011). In this respect, there has been a conflict of interest between ink manufacturer and printer on one side and the recycled paper consumers on the other side. The ink manufacturer and printer requires stronger attachment of the ink to the paper surface, but the paper recycling process needs easy and fast removal of the ink particles.

This conflict of interest has steadily intensified with the advent of digital printing technologies, which impose exceptionally high demand upon ink, paper, and the printing process (Li and He 2011). The increasing incorporation of mixed office waste in deinking recycled paper stock and the presence of the higher proportion of hard-to-deink non-contact printed material initiated intensive research to understand better detachment and separation of the ink particles (Thompson 1998; Lane *et al.* 2010).

Among various printing processes, inkjet printing has witnessed fast development as a non-contact printing process for high volume printing applications (Hladnik 2004; Nyman and Hakala 2011). Even though inkjet printed papers comprise only 10% of the total deinking recycled papers (Carre and Magnin 2004), this minor volume is already present in the mixture of recovered paper and its poor deinking potential imparts the worst threat so far to the deinking industry (Ingede 2008). Pigment-based inkjet inks are comprised of very finely divided and dispersed pigment particles in water, alcohol additives, and some binders (Oittinen and Saarelma, 2000; Carré and Magnin 2002). During the course of slushing of such printed papers, ink particles do not create dirt specks, but rather they release very fine ink particles (as small as 0.1 to 0.3 µm in diameter) to the surrounding water phase (Kemppainen *et al.* 2011). Inkjet inks contain hydrophobic dyes that do not agglomerate and cannot be removed efficiently, but these particles have the tendency to redeposit even inside the lumen of the fibers (Nyman and Hakala 2011; Kemppainen *et al.* 2011).

The complex structure of paper and its surface characteristics and physical chemistry will influence its printability, the bond strength of ink on fiber, and its de-inking behavior (Xu *et al.* 2005). Moutinho *et al.* (2011) emphasized the importance of paper surface chemistry on ink-jet printing. The effect of ink-jet paper roughness and topography on inkjet print (Li and He 2011; Xu *et al.* 2005) has been acknowledged. Li and He (2011) expressed that the printing performance and the print appearance is influenced by ink penetration into the subsurface of the paper and the paper topography is the critical factor for the penetration of the ink and the depth of penetration.

Recent reports have shown that refining, in addition to improving the strength properties of paper, contributes to surface characteristics and better fiber bonding (Fardim and Duran 2003; Bhardwaj *et al.* 2007; Perng *et al.* 2009). The primary effects of refining include internal and external fibrillation, fiber shortening, fiber flexibility, and higher inter-fiber bonding, as well as improvement in ink attachment to fiber surface and possibly penetration into the spaces between the fibrils (McKinney 1995). The external fibrillation delaminate the surface layer of the fiber that effect the fiber-fiber bonds as well as improving the retention of fillers, pigments, and colloidal particles in paper making (Fardim and Duran 2003).

Various aspects of the pulp refining on paper characteristics have been studied, but reliable research reports on the impact of refining on paper de-inking is limited. This study reports the effect of pulp refining on de-inking potential of inkjet printed paper and strength properties of deinked pulp to discover the relation between refining degree and ink to fiber bonding strength.

EXPERIMENTAL

Materials and Preparation of Handsheets

A mixture of 80% bleached Eucalyptus kraft market pulp and 20% bleached Scots pine market pulp (NBKP) was used. Pulps were refined according to TAPPI T248 sp-08 in a PFI mill, to reach 550, 430, and 340 mL CSF freeness, measured according to TAPPI T227 om-04. Then, from each pulp, 20 handsheets were produced according to TAPPI, T 205 sp-06 for ink-jet printing. Handsheets were made without adding any filler material. The fiber classification of the unrefined and refined pulps are measured and reported in Table 1.

Printing on Handsheets and De-Inking

Handsheets from each of the one unrefined and three refined pulps were randomly selected for printing with a HP Photosmart C5283 ink-jet printer, using pigment-based black ink, CB335HP140. To minimize the impact of print intensity, one text was selected for printing on all handsheets, and fresh cartridges were used to avoid the reduction of print intensity. For ink-jet printing, we used round handsheets, diameter 200 mm, and only one side of the handsheet was printed with about 200 words.

To measure the de-inking potential, samples of different HP ink-jet printed handsheets were selected for de-inking. Samples weighing 10 grams (oven dry) were de-inked using 2% hydrogen peroxide, 1% sodium hydroxide, 0.2% DTPA, 2.5% sodium silicate, and 1% sodium stearate. All chemicals were reagent grade supplied by Merck, Dormshtat, Germany.

Samples of printed paper were slushed at 4% consistency with tap water at 40 ^{o}C in a laboratory mixer (household mixer with modified rotor to simulate the laboratory pulp disintegrator). The mixer rotor speed was adjusted at 1000 rpm until the pulp suspension was apparently uniform. Then de-inking chemicals were added to the suspension, and mixing continued for another 10 minutes. The pulp suspension was kept without stirring for 20 minutes to provide sufficient time for chemical reactions. Then the detached ink was washed using a 120-mesh screen under continuous flow of tap water at 30^{o}C. During the washing process, inks, foam, and contaminants passed through the screen, and the de-inked fibers remained. Washing was carried out for 2 minutes, and then samples were de-watered and the deinking yield was measured. In pigment based inks, after the initial slushing of the inkjet printed paper, the particles do not agglomerate and cannot be removed efficiently by flotation (Nyman and Hakala 2011).Therefore, we used flotation chemistry to reach better detachment of the ink particles from the surface of the fibers, and since we anticipated that the detached ink particles were small, we used washing to separate the particles from the fiber slurry.

Roughness, Optical, and Strength Properties

Four handsheets from each de-inked pulp were randomly selected, and the strength and optical properties were determined according to relevant TAPPI test methods as follow: opacity, T 425 om-06; brightness, T 452 om-08; tear strength index, T414 om-04; and tensile strength index, T494 om-02. The surface roughness was also determined according to ISO 8791-4 (2MPa force).

Paper Printability and Ink Bond Strength

Four ink-jet printed handsheets from each freeness degree were randomly selected, and printing tests and ink junction strength of these printed handsheets were performed at MAN-ROLAND Laboratory, Germany. The printing test methods were the following:

Handsheets were scanned with UMAX Astra 1200S operating at 600 dpi in gray mode with gain correction of 88 percent. Then, the objects were measured using the appropriate software.

Solid area quality was evaluated using three metrics: optical density, black uniformity, and black mottle. Optical density was obtained from the translation of digital count data through a transfer curve relating scanner gray values and density values of a calibration target measured with a RD 1200 Macbeth® Densitometer Black Uniformity was evaluated by calculating the standard deviation of the gray averages of an array of 12 2mm × 2mm squares. Mottle was quantified by determining the number of light clusters with areas of 2 to 10 pixels and areas of 10 to 100 pixels (calibration: 1 pixel = 0.04298 mm) that were five gray levels different from the average gray value of the solid area. Higher numbers of clusters are indicative of solid areas that appear more uneven and mottled.

Text focus was assessed by calculating the sum of the squares of the differences in gray values of any two adjacent pixels (horizontal or vertical) within a region of interest placed over a block of text. A defined testing method is not available, and since 1989, a computerized method from Image Expert Inc. is used.

Pixel format, pixel pitch, yield points, contrast transfer function narrow vertical, black white vertical line width, letter area, and contact angle of the ink jet nip were analyzed with Design-Expert software by State-Ease. Finally, ink tension was measured using laboratory plasma surface treatment machine (Tantec).

Fiber analysis

The fiber length (weight average, mm), fines content (arithmetic, %), coarseness, curl, and kink index of the unrefined and refined pulps were analyzed using a fiber quality analyzer, (FQA, Opitest Equipment Inc, ON, Canada) (Fatehi *et al.* 2011).

Statistical Analysis

Analysis of variance (One Way ANOVA) was used for statistical analysis of the data, and a significant difference at the 99% level was observed. Then a mean separation using the Duncan Multiple Range Test (DMRT) was applied.

RESULTS AND DISCUSSION

Fiber Properties

The properties of unrefined and refined pulp fibers are listed in Table 1. Extensive changes were not imparted to the fibers upon refining, and all the properties reported in Table 1 were almost the same. This indicates that the impact of fiber characteristics such as the percentage of the fine is negligible in terms of handsheet properties.

Table 1. The Fiber Properties of Pulp Refined to Different Degrees (Pulp Mixture; 20% Scots Pine Kraft Pulp Fiber, 80% Eucalyptus Kraft Pulp Fiber)

Refining Degree (mL CSF)	Fiber Length, (LW),mm	Fines (%)	Curl	Kink index 1/mm	Coarseness, mg/g
650	1.03	40.2	0.11	1.18	0.49
550	1.04	41.5	0.1	1.04	0.46
430	1	39.7	0.12	1.16	0.49
340	1.03	40.4	0.11	1.09	0.47

Effect of Refining on De-Inking Potential of Hand Sheets

The yield, roughness, and optical properties of de-inked ink-jet printed handsheets produced using pulps unrefined and refined to different freeness levels are summarized in Table 2.

Table 2. Yield and Optical Properties of De-Inked Pulp Produced from Ink-Jet Printed Hand Sheets (De-Inking Chemical Dosage: NaOH; 1%, H_2O_2; 2%, DTPA; 0.2%, Sodium Silicate; 2.5%, Sodium Stearate; 1%)

Trial No	PFI (Rev)	Freeness (mL CSF)	Yield (%)	Brightness (%ISO)	Opacity (%ISO)	Roughness (µm)
1	0	650	95.55	96.13	34.07	6.95
2	6000	550	95.50	92.33	36.82	5.05
3	11000	430	94.85	92.83	36.54	4.55
4	14000	340	93.65	96.04	34.23	4.5

As was anticipated, de-inking eliminated part of the material while separating both ink particles and mainly fines from the pulp suspension. More refining reduced the de-inking yield by 1.9% (the de-inking yield of unbeaten pulp was measured as 95.55% and the yield of pulp beaten to 340 mL CSF was 93.65%). Since identical printing was applied on all handsheets, it can be concluded that more fines were rejected during washing. The effect of refining on de-inking yield was statistically significant at the 99% level ($p<0.01$). The maximum yield was reached while de-inking handsheets produced from unbeaten pulp and the lowest yield (93.65%) was related to de-inking handsheets made from pulp refined to 340 mL CSF (Table 2). Kemppanen *et al.* (2011) stated that inkjet ink particles after slushing redeposit not only on the fibers but also inside the lumen of the fibers. These redeposited particles cannot be removed without substantial fiber loss ending in lower deinking yield.

The effect of refining on the brightness of the de-inked pulps was statistically significant at the 99% level ($p<0.01$). The maximum brightness value (96.13% ISO) was generated from de-inking handsheets prepared from unrefined pulp (650 mL CSF), and the lowest value (92.33% ISO) was related to de-inked pulp from handsheets prepared from pulps refined to 550 mL CSF. We have used fully bleached market pulp for this study, and the sheets were not heavily printed. Therefore, the brightness of the deinked pulp is higher than usual deinked pulp. As seen in Table 2, the brighter deinked pulp was generated from the printed sheet produced from either unrefined or refined to 340 mL CSF. At the highest degree of refining, which was required to reach the lower freeness value (340 mL CSF), a smoother surface is produced, which inhibits the penetration of pigment particles into the sheet (Li and He 2011) and facilitates the separation of the ink particles in deinking process.

The opacity of the de-inked pulp followed the opposite trend compared to brightness. Lowest and highest opacity values were obtained from the pulps with 650 and 550 mL CSF, respectively (Table 2).

Pulp refining generates fibrillation on the outer surface of the fibers (Fig. 1), and ink particles, especially ink jet particles, penetrate the openings produced by such fibrillation (Li and He 2011; Kemppainen *et al.* 2011).

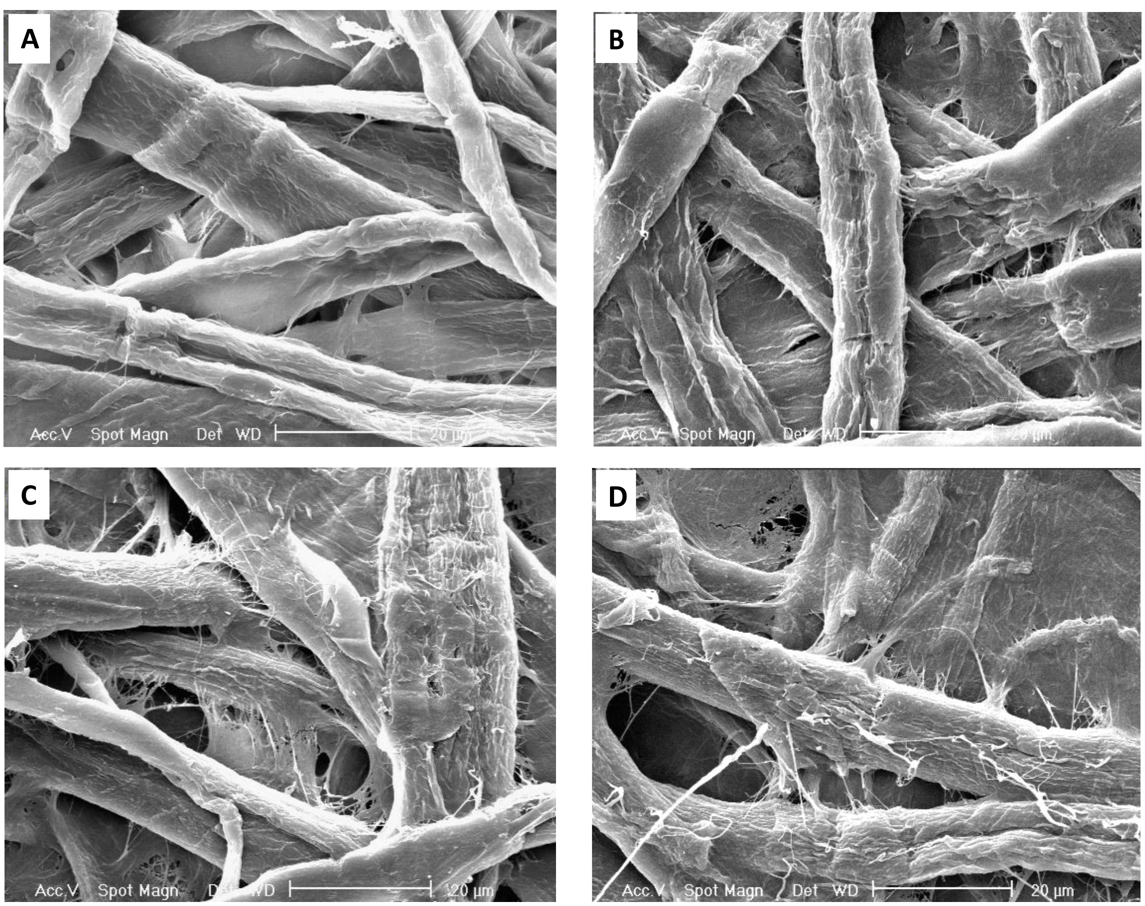

Fig. 1. SEM micrographs of fibers refined to different freeness (A; 650, B; 550, C; 430 and D; 340 mL CSF)

It has been acknowledged that penetration of ink particles into the fibrillation makes de-inking harder (McKinney 1995), and consequently the de-inking will be difficult. However, our study showed that at higher refining degree, the brightness development was better, which is attributed to two factors: (1) detachment of fibrils from the surface of the refined fibers and separation of the generated fines from the fibers; and (2) better felting of the fibers in the paper sheet to produce a smoother surface, which prevents deeper penetration of the inkjet ink pigment particles. We did not use any filler to avoid the impact of ash content on print quality and deinking, and since the fines content of the different pulps were almost similar, the effect of these variables can be ignored.

Effect of Refining on Printability and Ink Bond Strength

The results of printability and ink junction strength tests on refined handsheets are summarized in Table 3.

Table 3. Results of Printability and Ink Junction Strength Test on Handsheets Produced from Four Refined Pulps

Test	650 mL CSF	550 mL CSF	430 mL CSF	340 mL CSF
Black Optical Density	1.341	1.303	1.336	1.348
Black Uniformity (mm)	0.0062	0.0081	0.0051	0.0043
Black mottle 2-10 (No. of clusters)	193	202	199	190
Black mottle (10-100)	45	64	50	46
Yield points (%)	74.7	75.42	74.64	75.45
Text focus	189.5	184.4	192.1	191.2
Contrast transfer function narrow vertical	0.924	0.910	0.934	0.929
Black white vertical line width (mm)	0.495	0.499	0.494	0.490
Letter area (mm^2)	1.886	1.938	1.866	1.872
Contact angle of the ink nip (deg)	46.8	45.7	41.3	48.1
Ink tension	30±3 dynes/cm			
Ink junction strength on paper ($\Omega\ cm^2$)	$<1\times10^{-3}$	$<1\times10^{-3}$	$<1\times10^{-3}$	$<1\times10^{-3}$

The pulps were refined to different degrees, and handsheets with different surface roughness were produced. However, the printing characteristics of the handsheets did not vary significantly. It is believed that the surface roughness of the paper will influence the print quality. But within a narrow range of surface roughness, the impact of the roughness is not very significant, and other factors, such as paper surface chemistry, are more important (Moutinho *et al.* 2011), and other factors did not vary in our experiment.

The Strength Properties of the Unprinted and De-Inked Pulp

Tensile and tear strength of the paper before (unprinted) and after de-inking were measured, and results are shown in Fig. 2. Both tensile and tear strength indices of the papers increased upon refining the pulp to different freeness levels. Refining generates external fibrillation, which facilitates more fiber bonding and higher tensile strength. Even though the tear strength of paper usually is reduced due to refining, the possible removal of the fines during sheet forming and better felting and generation of stronger fiber network may improve the tear strength as well. In any case, it was expected that the tensile strength index of de-inked paper should be lower than unprinted papers. However, the separation and removal of the fines during washing and the swelling effect of NaOH used for deinking improved the tensile strength index of de-inked paper. The only exception was the handsheets made using the pulp refined to 550 mL CSF. The tear strength index of the de-inked pulps was lower than the unprinted samples, except for the unrefined pulp (650 mL CSF), in which the tear strength indices of deinked pulp was higher.

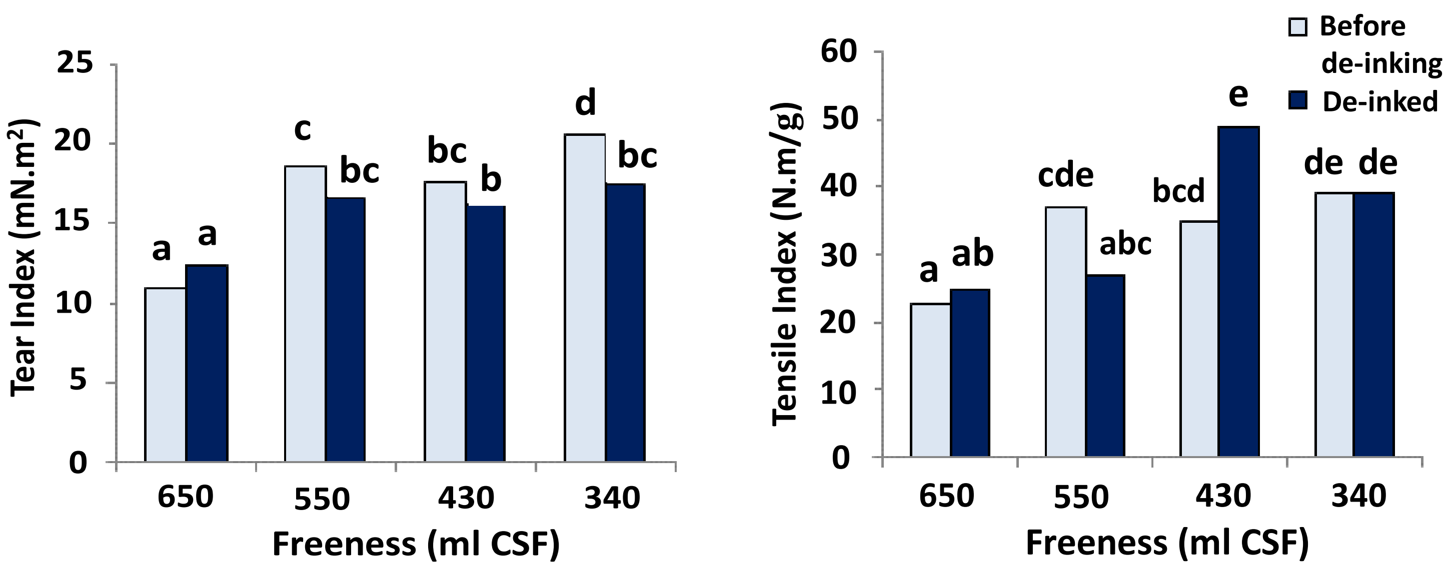

Fig. 2. The effect of refining on unprinted and de-inked paper strength (lower case letters indicates the DMRT grouping of the averages)

CONCLUSIONS

1. Despite the fact that it is estimated that the pigment based inkjet printed paper is only 10% of the mixed office waste papers intended for de-inking (Carré and Magnin 2004), this minor amount poses a serious threat in deinking processes, which require special measures to utilize this valuable portion of recycled paper.
2. Pulp refining will usually reduce the surface roughness of paper, and therefore the print quality will be better. It is believed that ink attachment to fibers will be stronger, which may adversely affect the de-inking potential. However, we have discovered that when bleached pulps were refined to lower freeness levels (340 mL CSF), the surface roughness was reduced marginally, but the brightness

development of de-inked pulp as an indication of de-inking potential was better compared to pulps refined to either 550 or 430 mL CSF. This may be the consequence of a denser surface and lesser voids on the paper made from pulp refined to 340 mL CSF.

3. At lower freeness levels, more fibrillation is generated and fine pigment particles are attached to these fibrils (McKinney 1995) and penetrate the microvoids in the fibers (Ben *et al.* 2000). However, these fibrils will break under the shear forces of slushing to produce more fines, which are separated during subsequent washing. The deinking yield is reduced.
4. The tear strength index of the paper increased after refining, but it was reduced upon de-inking due to the breaking of fibrils and generation of fines. On the other hand, for unrefined pulp (650 mL CSF), the tear strength index of unprinted paper was lower, but at higher degrees of refining, the tear strength indices of deinked papers was lower. However, we observed that at higher degrees of refining (freeness levels of 430 and 340 mL CSF), the tensile strength index of deinked papers were either higher or similar to unrefined papers.

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