The Influence of Refining History of Waste NSSC Paper on its Recyclability

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The effects of refining history and recycling times of NSSC pulp as a representative of semi-chemical pulps were studied. The results indicated that NSSC behaved as would be expected for a chemical pulp in all aspects. In fact, increasing the recycling cycles decreased the apparent density, tensile index, burst index, tear index, water retention value (WRV), and increased the hornification. In the current research, 400 mL CSF was judged to be the most suitable treatment among the refining levels considered. In the case of virgin pulp 400 mL CSF yielded better results than 500 mL CSF in all aspects (apparent density, tensile index, burst index, tear index, WRV and hornification). Also, there was not much difference with 300 mL CSF in these properties. Generally, a refining history of 400 mL CSF gave rise to the least negative influence on different properties compared to 500 and 300 mL CSF in 1st, 2nd, and 3rd recycling cycles of NSSC.

Keywords: Refining history; NSSC; Recycling cycle; WRV; Hornification

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INTRODUCTION

The global fiber demand for paper products is expected to increase substantially within the next decade. To meet these fiber needs, increasing the recovery and utilization of recycled fiber and optimization of virgin fiber yield by relying more heavily on high-yield mechanical pulping are some solutions (Moore 2008). During the past decades, numerous studies have been conducted on the potential of papermaking from recycled fibers (Mckee 1971; Cildir and Howarth 1972; Bovin et al. 1973; Szwarcsztajn and Przybysz 1976; Cardwell and Alexander 1977; McComb and Williams 1981; Van Wyk and Gerischer 1982; Bobalek and Chaturvedi 1989; Howard 1990; Howard and Bichard, 1992; Law 1996; Law *et al.* 1996; Bawden and Kibblewhite 1997; Hubbe *et al*. 2003a,b).

Loss in strength properties of recycled fibers compared to those of virgin fibers is a problem for the use of dried market pulp and recycled papers. Most studies have shown that the strength properties of fibers and paper are reduced upon recycling (Mckee 1971; Cildir and Howarth 1972; Bovin *et al.* 1973; Szwarcsztajn and Przybysz 1976; Van Wyk and Gerischer 1982; Bobalek and Chaturvedi 1989; Bawden and Kibblewhite 1997). By contrast, some reports have shown increases in some properties, especially in mechanical pulp recycling (Cardwell and Alexander 1977).

The change in basic fiber characteristics (strength, length, swelling, and bonding potential) has been assumed to be the source of reduction in strength properties (Ellis and Sedlachek 1993). Thus, one of the most challenging aspects of recycling lies in understanding how to increase and control fiber bonding potential (Wistara and Young 1999; Ellis and Sedlachek 1993).

The objective of this study was to investigate the effect of refining history of waste NSSC paper subjected to several recycling cycles on the properties of the recycled paper. Although different studies have considered the recyclability of various pulps (Mckee 1971; Cildir and Howarth 1972; Bovin et al. 1973; Szwarcsztajn and Przybysz 1976; Cardwell and Alexander 1977; Van Wyk and Gerischer 1982; Bobalek and Chaturvedi 1989; Howard, 1990; Howard and Bichard 1992; Law 1996; Bawden and Kibblewhite 1997), it seems that the type of wood from which the pulp is derived and the lignin content of the original pulps appear to have different effects on the changes in recycled pulp properties. As there has not been sufficient information about the behaviors of NSSC, this study has attempted to find the needed answers.

EXPERIMENTAL

Virgin NSSC pulp produced from mixed hardwoods (poplar, birch, beech, alder and hornbeam) was supplied from Mazandaran Pulp and Paper Mill. The pulp was stored in cold room with 30% consistency.

Table 1. Characteristics of NSSC Pulp

	Freeness (°SR)	Yield (%)	pH	Shives (%)
NSSC	15	77.7	6.5	2.2

The pulp was refined with a PFI mill refiner to three different levels of freeness (300, 400, and 500 mL CSF) according to the TAPPI method.

The handsheets were made with a KCL handsheet maker according SCAN-C M5:67 from the pulps with different refining levels. The handsheets were pressed and then dried in a drum drier at 90 °C. These sheets were named Virgin Paper. One-third of the sheets were chosen for determination of mechanical and physical properties. The others were soaked for 24 h in tap water and then repulped and disintegrated without subsequent refining. The handsheets were made from this pulp and named 1st recycling. This procedure was repeated twice more, and the handsheets were named 2nd recycling and 3rd recycling. The grammage (according to TAPPI T410 om-02), apparent density, tear index (TAPPI T414 om-04), burst index (TAPPI T403 om-02), and tensile index (TAPPI T494 om-01) were the mechanical properties which were measured. Also water retention value (Modified TAPPI UM-256), hornification, and fines content (SCAN-CM 66:05) were determined in this investigation.

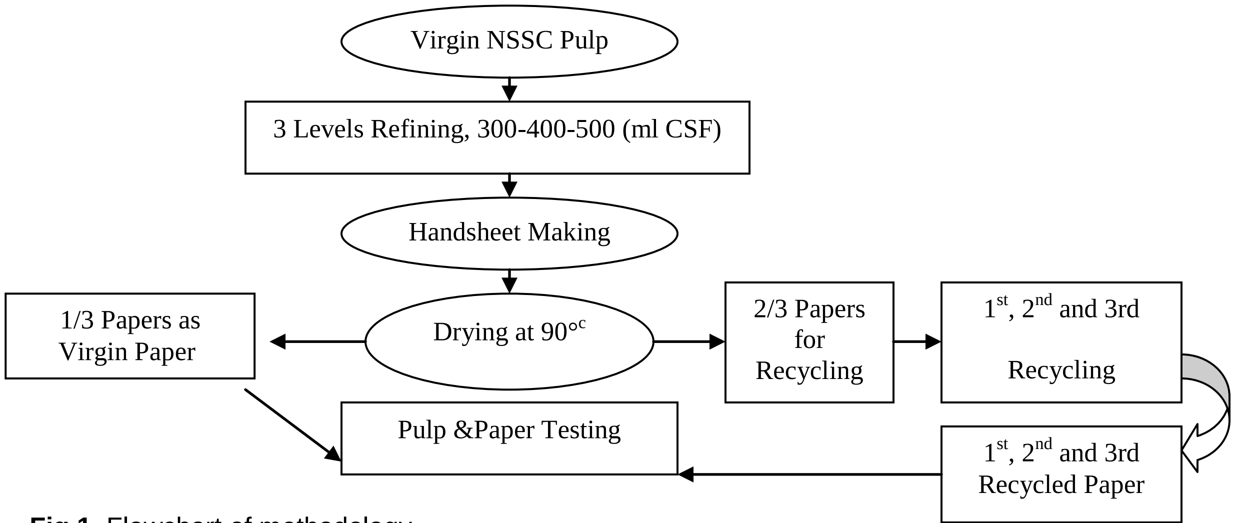

Fig.1. Flowchart of methodology

The results of the study were statistically analyzed using a completely randomized design, and Duncan's new multiple range test was used to categorize the averages.

RESULTS AND DISCUSSION

Effect of Refining History and Recycling Times of Waste NSSC Paper on Apparent Density of Recycled Paper

As shown in Fig. 2, in all recycling cycles the apparent density had an increasing trend with refining. Fibers after refining were flattened and made more flexible, and their bonding surface area was increased.

For virgin pulp (0 cycle), the highest apparent density was observed in the more refined pulp (300 CSF) because the network structure depends on collapsibility, conform-ability, and flexibility of the wet fibers. Conformable fibers bend and match the shape of each other to give a dense and well bonded network. In other cycles of recycling, the trends are identical to zero cycle; in each case the refining history was the main reason for this result. It seems that in each recycling cycle, recycled fibers that had a history of being subjected to more refining preserved their conformability and surface area to a greater extent compared to fibers which had lower refining history. The difference in response of fibers to refining, as indicated by the apparent density, was more obvious between 400 and 500 mL CSF.

The results indicated that refining had greater effectiveness between 400 and 500 mL CSF, and the loss of fiber-to-fiber bonding was more obvious in this range. Through the recycling cycles, there was a slightly decreasing slope towards the third cycle, although it was not so obvious. The decreasing of fibers being able to achieve interfiber contact and thus fiber-to-fiber bonding may be the reason for these results.

With reference to the above-mentioned results, the NSSC pulp in this process was found to act similarly to chemical pulps (Mckee 1971; Bobalek and Chaturvedi 1989; Kim et al. 2000; Yamauchi and Yamamoto 2008). Law (1996) also showed slight decreasing of apparent density in recycling of CMP and CTMP papers up to fifth cycle.

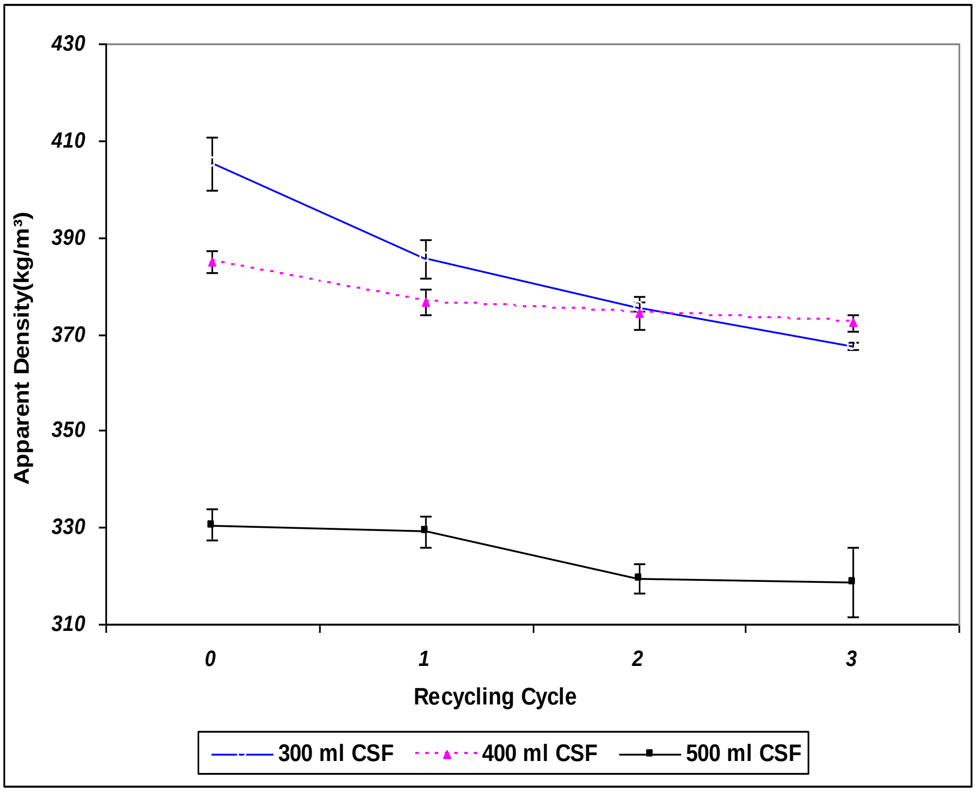

Fig. 2. Effect of refining history and recycling times of waste NSSC paper on apparent density

Effect of Refining History and Recycling Times of Waste NSSC Paper on Tensile and Burst Indices of Recycled Paper

As shown in Fig. 3, the highest tensile index (about 40 Nm/g) was observed in the zero cycle (virgin pulp) with 300 mL CSF refining. The corresponding tensile index results for 400 and 500 mL CSF followed after 300 mL CSF, respectively. This trend in virgin pulp was the same as what was found in some other studies (García *et al.* 2002; Kim *et al.* 2000). This result may be because of having better bonding potential in virgin pulps. In the 1st and 2nd recycling cycles, the highest results of tensile index were in 300, 400, and 500 mL CSF cases, respectively. As mentioned above, such results can be attributed to refining history as the main reason. This is in contrast to certain earlier results that showed refining history did not appear to play a significant role relative to strength loss or pore closure (Hubbe *et al*. 2003a). However Bobalek and Chaturvedi (1989) concluded that decrease in strength is positively correlated to the extent that the fibers undergo refining during in their first use, particularly for softwoods.

By increasing recycling cycles, decreases in tensile index can be seen. The decreasing of fibers potential in formation of bonding may be the reason behind these results. The loss of bonding ability may be associated with effectively irreversible closure of pores within the cell walls of the fibers (Hubbe *et al*. 2003b). However, according to Gurnagul *et al.* (2001) in the once-dried pulps the primary cause of tensile strength reduction upon drying is the loss of shear bond strength, with a minor reduction caused by a loss in the bonded area.

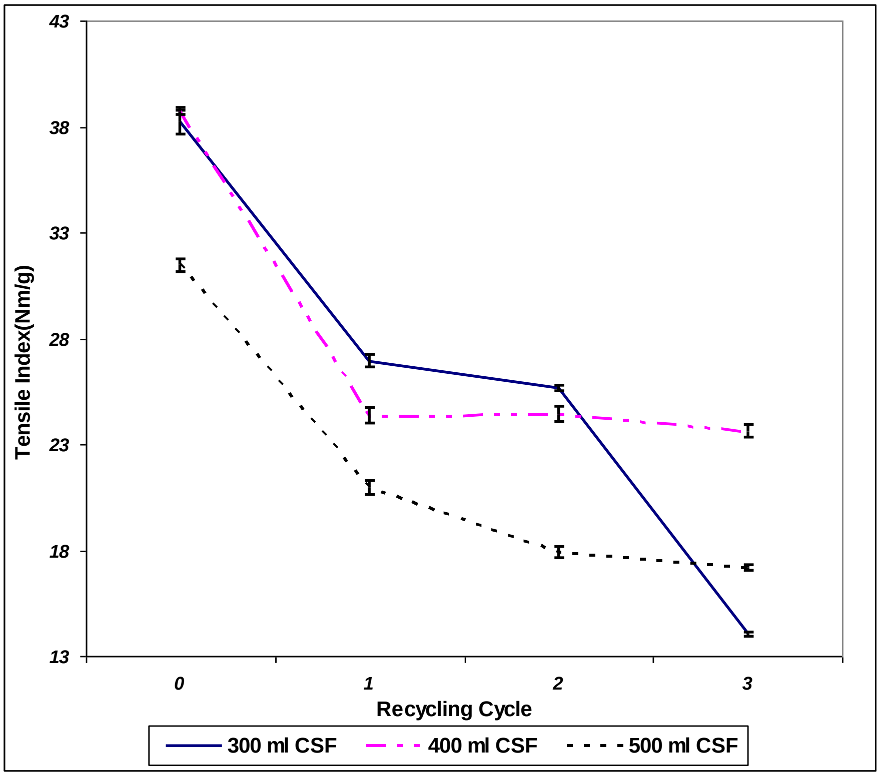

Fig. 3. Effect of refining history and recycling times of waste NSSC paper on tensile index

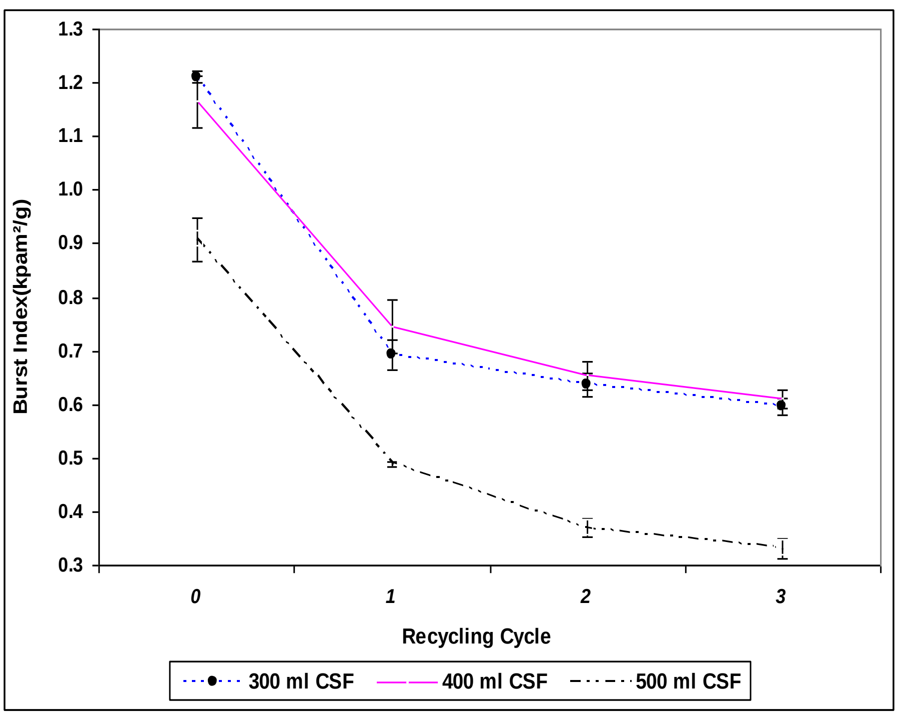

Fig. 4. Effect of refining history and recycling times of waste NSSC paper on burst index

In fact, the NSSC pulp was found to act similarly to chemical pulps (Mckee 1971; Cildir and Howarth 1972; Szwarcsztajn and Przybysz 1976; Van Wyk and Gerischer 1982; Bobalek and Chaturvedi 1989; Howard and Bichard 1992) and some mechanical pulps (Law 1996; Law *et al.* 1996; Jahan 2003; Kang and Paulapuro 2006; Yamauchi and Yamamoto 2008).

Figure 4 indicates the effect of refining history and recycling times of waste NSSC pulp on burst index of recycled paper. The results parallel the findings for tensile index.

Effect of Refining History and Recycling Times of Waste NSSC paper on Tear Index of Recycled Paper

According to Fig. 5, at all refining levels the tear index decreased with increasing number of recycling times. Several factors such as "degree of bonding between fibers" and "fibers length" affect the tearing strength of paper. The former has been concluded to influence the decreasing trend of this property by the changes observed in both tensile and burst strength.

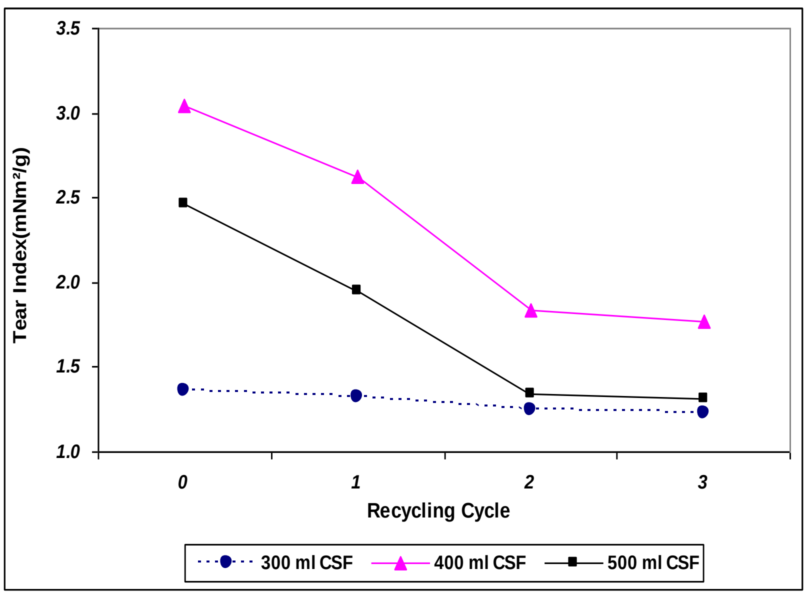

Fig. 5. Effect of refining history and recycling times of waste NSSC paper on tear Index

In order to estimate the effect of fiber shortening during the progression of fibers through several recycling cycles, fines content measurements were carried out. As shown in Table 2, the recycling sequence increased the average fines content of fibers in all freeness levels. These results are in contrast with results obtained for some mechanical pulps (Law 1996; Law *et al*. 1996; Howard and Bichard 1992; Jahan 2003) and some chemical pulps (Mckee 1971; Van Wyk and Gerischer 1982; Howard and Bichard 1992) but are in accord with some other reported findings (Cildir and Howarth 1972). However, this trend was not obvious in pulp with 300 mL CSF refining history, for which it is assumed that virgin pulp refining to the target freeness of 300 mL CSF imposed maximum fiber shortening to the extent that this property is less affected by fines generation over the course of several recycling cycles.

Table 2. Fines Content *vs*. Recycling Sequences and Final CSF

Freeness (CSF, mL)	Recycling Sequence (Times)	Avg. Fines Content * (%)
500	0*	12.09
	1	16.01
	2	17.43
	3	21.35
400	0	8.50
	1	13.89
	2	17.08
	3	16.08
300	0	12.59
	1	16.30
	2	19.22
	3	19.99

*All pulp samples were soaked in tap water for 30 hours before disintegration.
*The measurements were carried out in 3 replicates.
* Zero recycling sequence denotes "virgin" pulp.

The trend of tear index among different refining history, in all recycling cycles, was the same. The highest values for this property were observed in pulp with 400 mL CSF refining history. In fact, increases in tear index can be observed from 500 to 400 mL CSF and then decreasing from 400 to 300 mL CSF. This trend was the same as some others have reported (Seth 2001). As in previous findings, tear is related to three main factors, fibers length, strength of each fiber, and the bonding ability of fibers. In virgin pulp, the pulp with 500 mL CSF has proper length but because of mild refining the bonding ability of fibers did not improve so much compared to 400 mL CSF. As a result, the tear index of pulp refined up to 400 mL CSF was higher than 500 ml CSF. But in pulp refined up to 300 mL CSF, more extensive refining caused the paper sheet to become more brittle and failure occurred within a smaller zone within the sheet. As a result, less energy is consumed in tearing the paper. In the 1st, 2nd, and 3rd recycling cycles, the trend was the same as for the virgin cycle. In fact, the pulps history, preserved its effects, as seen for the other cycles.

Effect of Refining History and Recycling Times of Waste NSSC Paper on WRV and Hornification

As shown in Fig. 6, by increasing the recycling times, a slight decreasing trend in WRV was observed for different levels of refining history. Law (1996) and Law *et al*. (1996) observed a similar trend for mechanical pulp, but most of research has shown the same result for chemical pulps (Cildir and Howarth 1972; Szwarcsztajn and Przybysz 1976; Bawden and Kibblewhite 1997; Kim *et al.* 2000; Röder and Sixta 2004; Welf *et al*. 2005; Kang and Paulapuro 2006; Brancato 2008; Yamauchi and Yamamoto 2008).

Comparing the refining levels, there wasn't any obvious difference in virgin pulp. This trend was the same in the 1st recycling cycle. But in 2nd and 3rd recycling cycles, the pulp with 300 mL CSF refining history showed the largest adverse effect. In other words, the more intense refining gave rise to more WRV reduction after recycling. Several mechanisms have been suggested for WRV reduction in drying-wetting cycles.

The CLSM micrographs showed that the fibers subjected to the recycling treatment had inferior re-swelling capability and conformability and they could not achieve good interfiber contact in recycled handsheets (Somwang *et al*. 2002). Partial closure of pores in the fiber wall, especially most of the large pores and a substantial amount of the small ones, has been reported to be the main cause of WRV change (Wang 2006).

Another mechanism proposed to explain hornification is the reorganisation of the fibre cell wall structure. According to Clark (1978), when adjacent surfaces of cellulose and hemicelluloses previously separated come into contact upon drying, the process results in the creation of additional crystalline zones that prevent the separation of the two surfaces. Oksanen *et al*. (1997) demonstrated further that the removal of xylan and glucomannan is responsible for the decrease of the WRV of dried kraft pulps and suggested that hemicelluloses present in the fiber pores and in the interfibrillar spaces hamper hornification.

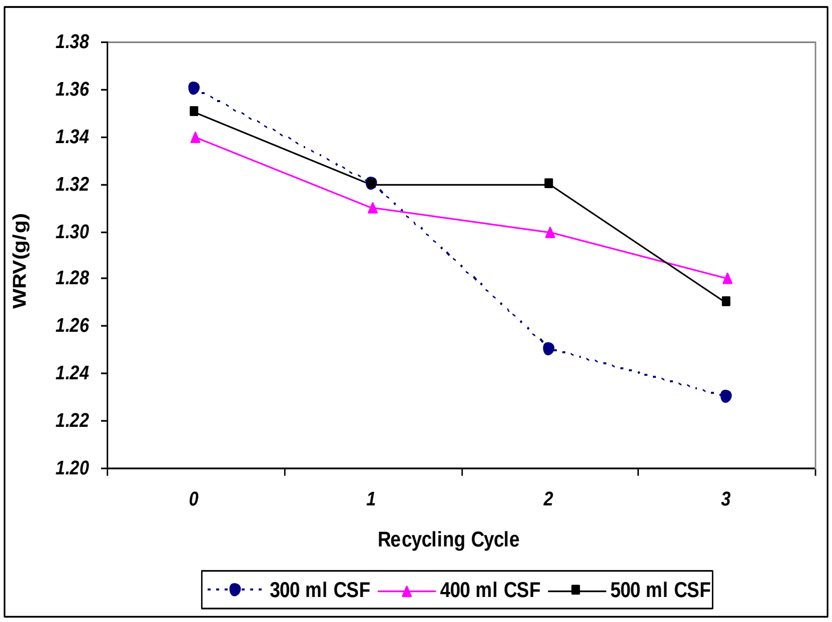

Fig. 6. Effect of refining history and recycling times of waste NSSC paper on WRV

According to Fig. 7, the trends for hornification were opposite to those obtained for WRV. Once-dried sheets almost had an identical hornification, while in the subsequent recycling cycles, intensively refined pulp (300 CSF) showed the highest hornifcation. Comparing Figs. 7 and 3, the main reason for the loss in fiber-to-fiber bonding was hornification of fibers in wetting-drying cycles. The effect of hornification on changes in strength properties of paper, though, has not been expressly proved so far (Šutý *et al.* 2008); however, many authors have pointed that hornified fibers are relatively stiff in the wet state, resulting in paper with inferior strength properties (Higgins and McKenzie 1963; Wistara and Young 1999; Hubbe *et al*. 2007).

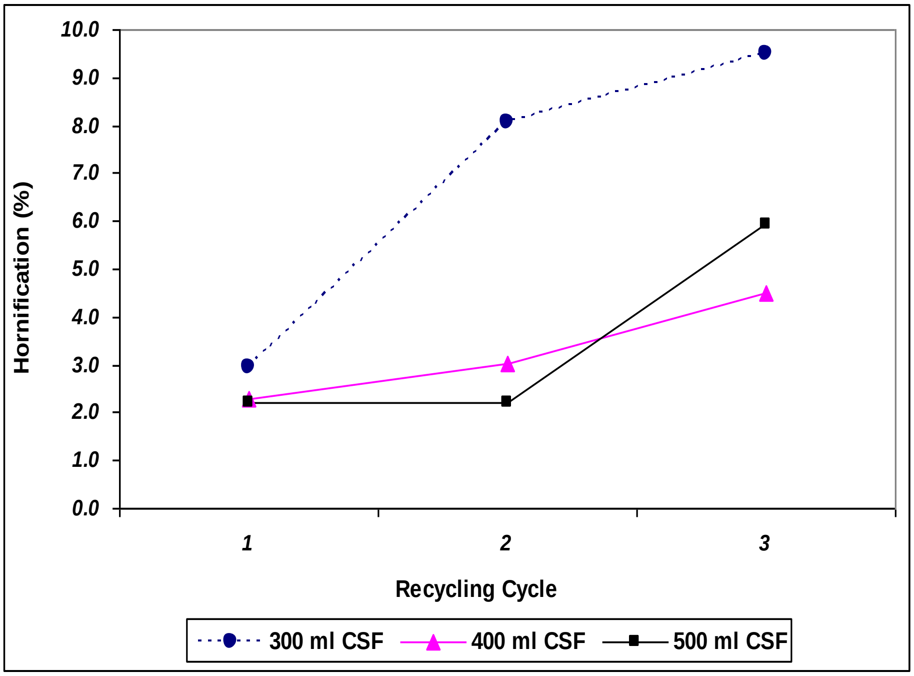

Fig. 7. Effect of refining history and recycling times of waste NSSC paper on Hornification

CONCLUSIONS

1. The results indicate that neutral sulfite semichemical (NSSC) pulp acts as a chemical pulp in all aspects. In fact, increasing the recycling cycles decreases the apparent density, tensile index, burst index, tear index, and water retention value (WRV) and increases the hornification.
2. It seems that the changes are irreversible.
3. Virgin pulp initially refined to 400 mL CSF performed better in all respects than pulp initially refined to 500 mL CSF (apparent density, tensile index, burst index, tear index, WRV, and hornification. Also, it did not show so much difference with 300 mL CSF in these properties.
4. Refining history of 400 mL CSF pulp exhibited the least negative influence on different properties compared to 500 and 300 mL CSF in the 1st, 2nd, and 3rd recycling cycles of NSSC.
5. According to the results mentioned above, the 400 mL CSF refining level can be selected because of better results in virgin pulp comparing 500 mL CSF, saving energy and other costs related to refining compared to 300 mL CSF and fewer effects on recycled pulp properties in subsequent recycling.

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