

Improving TMP rejects refining through alkaline peroxide pretreatment for value-added mechanical papers

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ABSTRACT: Pilot plant trials were conducted to clarify the effect of alkaline peroxide pretreatment on TMP rejects. Different alkaline and peroxide charges were applied to the rejects before refining. The studies showed that a 2.2% total alkali charge was not sufficient to achieve noticeable energy reduction or physical property improvement. However, at a total alkali charge of 5.2%, alkaline peroxide pretreatment reduced the specific refining energy by 20% to a given freeness, and increased pulp density and tensile strength, most likely as a result of increased fiber flexibility and conformability. With a peroxide charge of 2.9%, the brightness of the refined rejects reached 72%. However, alkaline peroxide pretreatment decreased light scattering and pulp yield.

Application: This study evaluates processes that may help mechanical pulp mills improve efficiencies and pulp quality.

Mechanical pulps play an important role in the paper industry, not only because of their much higher yield and lower environmental impact than chemical pulps, but also because of their unique pulp properties such as high bulk, high light-scattering coefficient, and high opacity [1]. On the other hand, the presence of lignin causes lower sheet strength and reduces the maximum brightness that can be achieved.

In a mechanical pulping process, rejects from screening and cleaning systems contain mainly long fibers and fiber bundles. Rejects refining is a critical step in achieving the desired pulp quality for mechanical value-added papers. The objective of rejects refining is to maximize long fiber strength and to optimize these long fibers for surface properties. One means of promoting this would be a chemical treatment, which would make fibers more flexible.

There are a number of studies on sulfonation of rejects [2–7], but very limited reports on alkaline peroxide pretreatment of rejects. Most of the work was reported by Strunk and his colleagues on southern pine thermomechanical pulp (TMP) and stone groundwood (SGW) rejects for newsprint [8–11]. In general, 10%–25% reduction in energy to a given freeness was observed by pretreating rejects with alkaline peroxide. A retention time of 40 min and a temperature of 60°C was found necessary to obtain maximum improvements in pulp properties [9]. When southern pine TMP rejects with a freeness of 462 mL were treated with 4% NaOH and 2% H₂O₂, the tensile index was increased by 20% and the shives content reduced by 50%. However, the bulk was reduced by 18%. Further increase in alkali charge up to 8% did not affect the pulp bulk and tensile

strength [9]. In a separate report [11] for southern pine TMP rejects with a higher freeness of 670 mL, 8% NaOH was required to get the same 20% increase in tensile. Also, only 10% decrease in bulk was found with 8% NaOH. Compared with TMP, alkaline peroxide pre-treatment had a larger impact on SGW rejects [8]. When the rejects were treated with 7.5% NaOH and 3% H₂O₂, the burst and tensile increased by 50%. This was accompanied by 25% decrease in refining energy. However, the pulp yield was decreased by 1% with every percent alkali used.

For a southern pine TMP newsprint furnish, 4% alkaline peroxide pretreatment of the rejects would allow a reduction of kraft pulp addition from 25% to 15% while maintaining paper strength properties [9]. No data were available for high value-added mechanical paper grades such as supercalendered (SC) and lightweight coated (LWC).

There is an increasing interest in alkaline peroxide pretreatment of rejects for LWC, SC, and other mechanical high-value papers, due to the potential of reducing refining energy and kraft pulp usage, as well as increased demand on pulp quality

WOOD SPECIES	SPRUCE/FIR
Consistency (%)	37.6
Canadian Standard Freeness (mL)	399
FQA fiber length (lw, mm)	1.68
ISO brightness (%)	58.6
FQA coarseness (mg/m)	0.18

I. Key properties of the TMP rejects (FQA = fiber quality analyzer).

such as low fiber coarseness, high fiber flexibility, and low shives content. The high surface requirements of these mechanical high-value papers make the condition of long fibers critical. The negative effect of chemical pretreatment of rejects is reduced opacity and bulk, but this may be compensated for by the reduction of kraft reinforcement pulp in the furnish, addition of fillers, less calendering, etc. The balance of the benefits and the detriments requires some systematic research into this area. Compared with newsprint, the mechanical high-value papers have a much higher rejects rate and are usually heavily calendered to achieve target surface properties. Therefore, the alkaline peroxide pretreatment on rejects could have a larger impact on these high-value papers.

The objectives of this study are: 1) to clarify the effects of alkaline peroxide pretreatment on TMP rejects, such as refining energy consumption, long fiber development, and pulp properties and 2) to examine the effect of chemically modified rejects on SCA paper properties when the rejects are combined with mainline accepts and kraft. This paper focuses on the first objective and a subsequent paper will report the results on the second objective.

EXPERIMENTAL

Raw Materials

The TMP screening and cleaning rejects were obtained from an eastern Canadian paper mill and sampled at the dewatering screw press prior to the rejects refiner. **Table I** shows the key properties of the rejects.

Alkaline Peroxide Pretreatment Before Refining

The TMP rejects were pretreated with alkaline peroxide before refining. A control run was also done by pretreating the rejects with water at the same temperature and retention time. Target chemical charges on oven dried (o.d.) rejects were 2%–7% NaOH and 2.5%–4% H_2O_2 , together with 3% silicate, 0.05% MgSO_4 , and 0.3% DTPA as stabilizers for the alkaline peroxide solution. The rejects and the chemical solution were mixed by passing the rejects through an atmospheric 36 in. double-disk refiner (Bauer 400) with the gap wide open. The rejects mixed with alkaline peroxide were retained in a plastic container at ~65°C for 30 min. Pulp samples were taken every 10 min to measure the pH and H_2O_2 residues in the pulps.

Refining

After retention, the treated rejects were refined in the same refiner using approximately 1200 kW•h/ton specific refining energy in the first stage, and then four different energy levels in the second stage. The lowest freeness target of the refined rejects was controlled at about 50 mL and the consistency after the second refining stage was around 20%. Pulp samples were collected at each energy level and were quick-

ly soured in a sodium meta-bisulphite solution to pH around 6. Again, samples were taken to measure the pH and H_2O_2 residues.

Pulp Testing

The pulp samples were thoroughly washed, screened, and latency removed before testing. Fiber length and coarseness were measured by a fiber quality analyzer (FQA). Pulp tests were done according to PAPTAC standard methods. The content of carboxylic acid groups of the refined rejects was measured by the published method [12].

Rejects Yield And Effluent Load

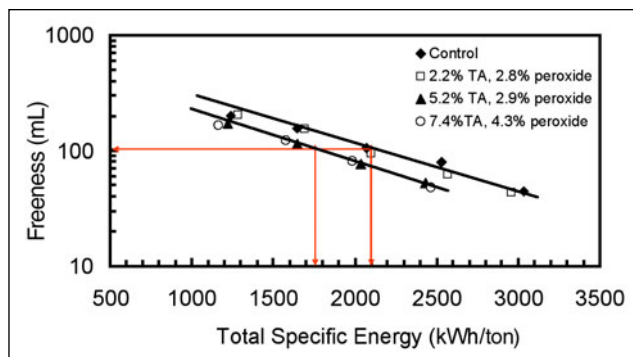
The yield of rejects after alkaline peroxide pretreatment was determined as follows: 30g o.d. unrefined sample was mixed with bleaching chemicals in a Hobart mixer for 5 min and then transferred to a plastic bag. The pulp consistency was adjusted to 28% and the bag was kept in a water bath for 30 min at 65°C. After a vigorous disintegration in 3 L de-ionized water using a Waring blender, the pulp slurry was filtered through a 150-mesh screen with recirculation until the filtrate became clear. The disintegration was repeated with 3 L fresh de-ionized water and the pulp slurry was left overnight. The slurry was filtered again the next day until the filtrate became clear. All the filtrate was collected and the total solids content was measured which was used in the mass balance later. The pulp pad was put into an oven and dried to a constant weight.

The effluent load was determined using a similar procedure to that described above. After the treatment under the specified conditions (65°C, 30 min), the sample was diluted to 5% consistency in a beaker and soured with sodium meta-bisulfite to a pH of around 6. The slurry was filtered through a 150-mesh screen with recirculation until the filtrate became clear. The filtrate was filtered through a Millipore® membrane again and bubbled with air for 40 min to remove any residual sodium meta-bisulfite. The collected samples were tested for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). BOD and COD determinations were done according to PAPTAC methods H.2 and H.3, respectively. TOC was measured using a Shimadzu TOC-V total organic carbon analyzer.

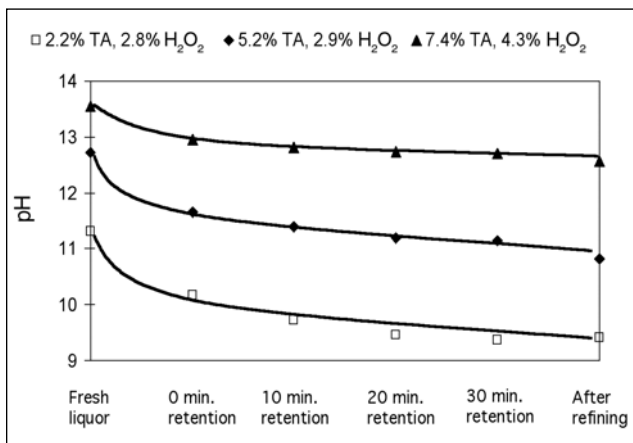
RESULTS AND DISCUSSION

Specific energy consumption

Figure 1 shows that at a total alkaline charge (TA) of 5.2%, the alkaline peroxide pretreatment on the TMP rejects can reduce the refining energy required to produce pulp at a freeness of 100 mL by 20%. Energy reduction of 10% to 25% to a given freeness was reported when southern pine TMP rejects were pretreated with 4.8% to 8.8% total alkali and 1.8% to 2.8% peroxide [9]. Groundwood rejects of southern pine and cottonwood also showed a similar response to al-



1. Alkaline peroxide pretreatment on TMP rejects reduced refining energy to a given freeness when the total alkali charge was 5.2%. No further reduction in refining energy was obtained when the total alkali charge (TA) was increased to 7.4%



2. pH profiles during alkaline peroxide pretreatments. Compared with the pretreatment with 5.2% or 7.4% total alkali charges, pretreatment with a 2.2% total alkali had a lower pH during the 30 min retention and a lower ending pH close to 9.

kaline peroxide pre-treatment when pre-treated with 7.5% NaOH and 3% H_2O_2 [8]. The decrease in refining energy is most likely due to the fact that under alkaline conditions, fibers swell more than those treated with water only [12–14]. Figure 1 also shows that increasing the total alkali charge to 7.4% did not lead to a further energy reduction. At a 2.2% total alkali charge, the freeness to specific energy relationship was the same as that of the control. This can be attributed to a low swelling degree at a low pH, as supported by the pH profile during alkaline peroxide pretreatment in **Fig. 2**. Compared with the pretreatment with 5.2% and 7.4% total alkaline, treatment with a 2.2% total alkali had a much lower pH during the 30-min retention time and a lower ending pH at 9. Similarly, it was reported that an alkaline peroxide pretreatment on groundwood rejects of south-

ern pine and cottonwood had a negligible effect on energy consumption when the caustic charge was 4.5% [8].

Pulp Properties

The alkaline peroxide pretreatment did not show a significant impact on the fiber size distribution after refining. This is in agreement with the reported results on southern pine TMP rejects [9]. However, the alkaline peroxide pretreatment reduced the fiber coarseness of the long fibers (Bauer-McNett P14/R28 fractions) as shown in **Fig. 3**. Fiber coarseness influences a wider variety of pulp properties than does fiber length, especially those relating to the surface quality of printing papers [15]. A typical caliper for SCA is 50 μm and the uncollapsed mechanical fibers may exceed half the sheet thickness of SCA [16]. In addition to the apparent influence on smoothness, stiff and uncollapsed mechanical long fibers in LWC and SC furnishes could be collapsed and stressed during calendering and later cause surface roughening upon rewetting in the coating or printing process. The implication of alkaline peroxide pretreatment on surface roughening will be discussed later in this paper.

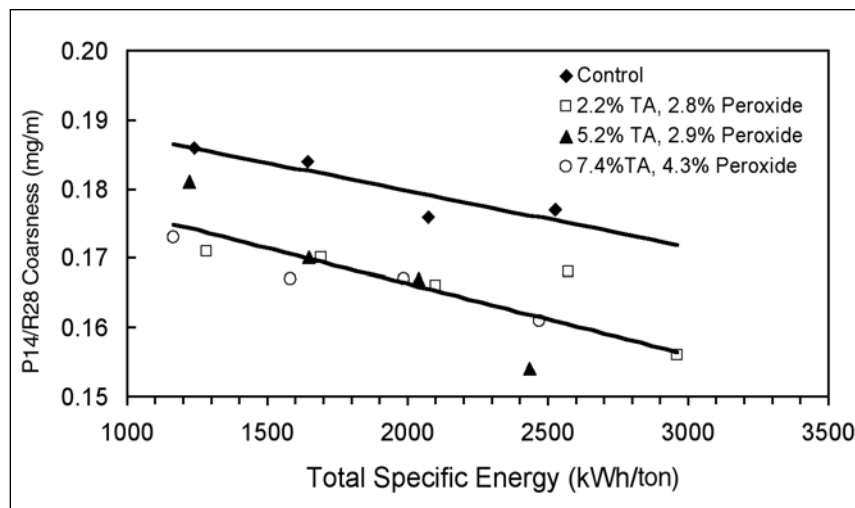
Figure 4 shows that the alkaline peroxide pretreatment significantly reduced the pulp bulk, especially at a higher total alkali charge. Compared with the control at the same refining energy, rejects treated with 5.2% and 7.4% total alkali charges reduced bulk by about 17% and 21%, respectively. Since the fiber size distributions were not affected by the alkaline peroxide pretreatment. The lower bulk due to the alkaline peroxide pretreatment is most likely the result of increased fiber flexibility and conformability. This is further supported by **Fig. 5**, which shows that the same values of bulk were reached at a higher long fiber content, an indication of more flexible and conformable long fibers for the pulps pretreated with alkaline peroxide [17].

It is well known that under an alkaline condition, in particular in the presence of hydrogen peroxide, carboxylic groups are generated on the pulp fibers due to the hydrolysis of hemicellulose and the oxidation of lignin [12,18–21]. These new acidic groups caused a higher ion concentration in the cell wall than the outside aqueous phase, and thus increasing the osmotic pressure which would draw additional water into the cell wall. Due to the swelling of the cell wall, fibers were softened and became more conformable. Tchepel et al. found that alkaline peroxide treatment reduces the fiber cross-sectional dimension which increases the flexibility of single fibers by lowering the amount of inertia [21]. It was reported that the fiber swelling was linearly related to alkali consumption [12]. At the same refining energy of 2000 $kW \cdot h/ton$, **Fig. 6** shows that the carboxylic content of the pulps increased with the total alkali charge. The decrease in bulk also helped decrease the air permeability of the pulps as shown in **Fig. 7**. The higher the total alkali charge, the lower the air permeability. Low air perme-

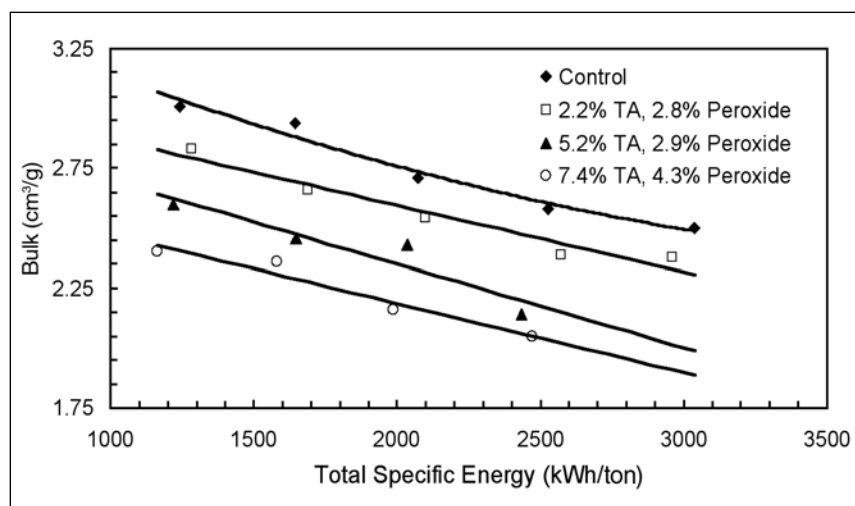
ability is desirable for SC and LWC papers. For example, lower air permeability will give a better coating hold-out for LWC paper.

At a given specific energy or freeness, the tensile energy absorption (TEA) was higher when the rejects were pretreated with total alkali charges of 5.2% and 7.4% compared to that of the control or rejects treated at a total alkali charge of 2.2%, as shown in **Fig. 8**. Moldenius [22] reported that there is a critical initial pH of 11 below which the strength properties of spruce mechanical pulps are not affected by the alkaline peroxide bleaching. Similar observations were also made by others [14,23,24]. In our study with a total alkali of 2.2%, although the initial pH is 11.3, slightly above 11, there was no strength improvement due to the alkaline peroxide pretreatment. This discrepancy could be explained by the fact that the pH dropped quickly to 10.2 after 1 min and then stayed at about 9.5 after 2 min of retention, as shown in Fig. 2. The rapid drop of pH in this case could be mainly attributed to the fast peroxide consumption. The pH profile during bleaching was not reported in Moldenius's report [22], but the decomposition of peroxide in his study is expected to be slower than in our study since his pulp was chelated before bleaching and the bleaching was done in the lab with deionized water and as much as 5% silicate.

The irreversible roughness increase, i.e., the surface roughening, is observed during coating and printing when water is applied onto the paper. This negatively affects the gloss and surface roughness of the final paper. It is generally believed that surface roughening occurs due to the debonding of mechanical long fiber and the recovery of its original tubular shape upon the release of internal stress induced by calendering [4,25–28]. It has been shown that increasing the proportion of long mechanical pulp fibers



3. Alkaline peroxide pretreatment reduced the coarseness of long fibers.

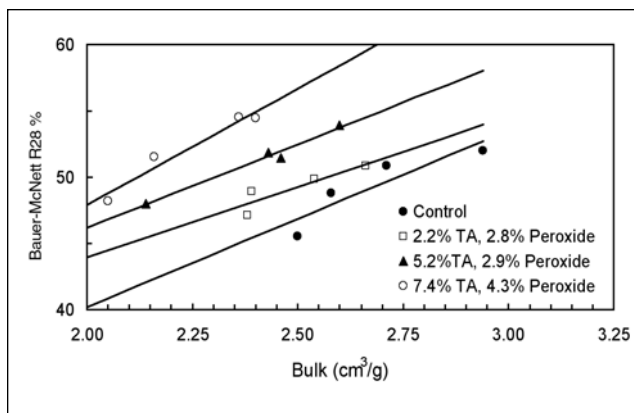


4. The alkaline peroxide pretreatment significantly reduced the pulp bulk, especially at a higher total alkali charge.

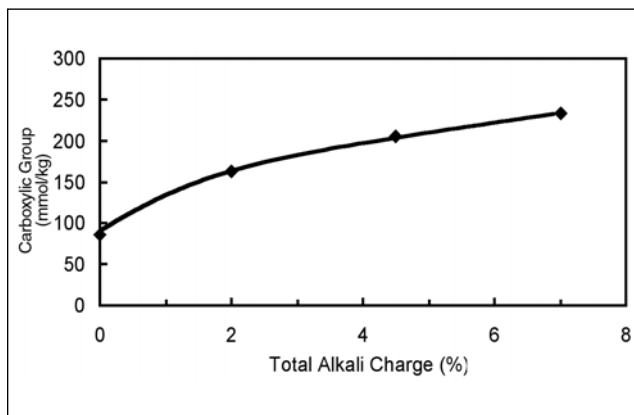
in the LWC base sheet did not increase the print roughness if the long fibers were thin-walled, flexible, and well bonded [26]. Since alkaline peroxide treatment improved inter-fiber bonding, reduced fiber coarseness, and increased fiber flexibility, this is expected to help reduce surface roughening of the high-value mechanical printing papers. Nurminen [4] has shown that sulfonation of TMP screen rejects helped reduce surface roughening in printing of LWC paper.

Figure 9 shows that alkaline per-

oxide pretreatment led to a decreased tear index at a total alkali charge higher than 2.2%. Tear index is mainly affected by the long fiber content in the paper (fiber length), fiber strength, and inter-fiber bonding. For those rejects pretreated with a 5.2% total alkali charge or higher, their long fiber fractions (R14+P14/R28) were similar to or even higher than the untreated rejects at the same energy levels. Fiber strength, which is usually reflected by the zero-span breaking length (**Fig. 10**) is also similar or higher than the

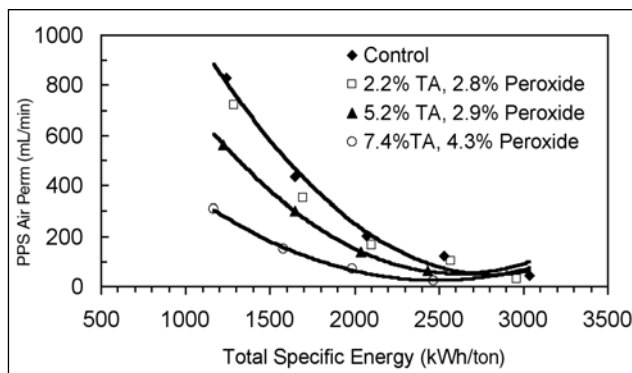


5. The same values of bulk were reached at a higher long fiber content, an indication of more flexible and conformable long fibers for the refined rejects pretreated with alkaline peroxide.

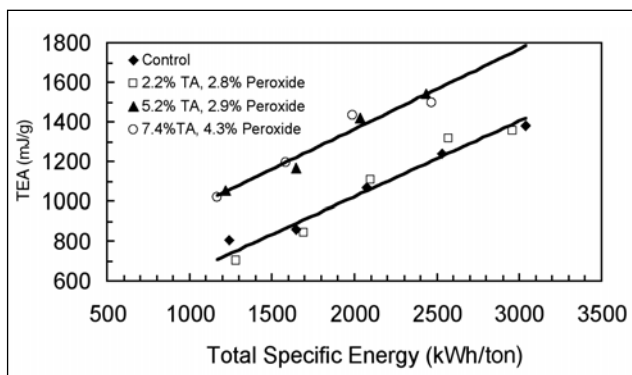


6. The carboxylic content of the refined rejects increased with the total alkali charge. The measurement of the carboxylic group was done on the rejects refined at a refining energy of 2000 kW.h/ton.

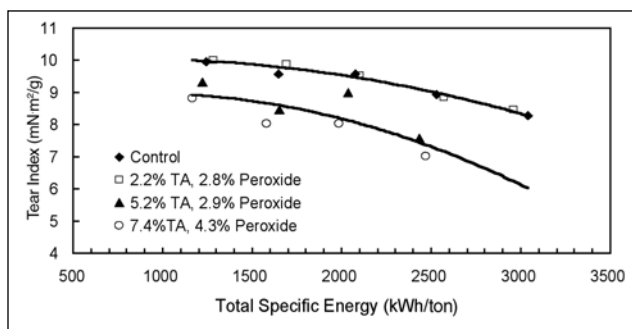
control for those pulps pretreated with a 5.2% total alkali charge or higher. The decrease in tear index can therefore be attributed to the improved fiber flexibility which led to a higher sheet density and better inter-fiber bonding. This will cause fiber breakage rather than pull-out during fracture [29]. **Figure 11** shows that tear index decreased with the increase in tensile index. Sulfonated TMP rejects after refining also showed a reduction on tear index [5]. Although the treated rejects had 6.2% higher long fiber (>R30) fraction, its tear index was decreased by 21.7%, compared to the control. Uesaka and his co-workers [30,31] have shown that tensile strength and uniformity are more significant factors than cross direction (CD) tear in affecting pressroom runnability. Therefore, the alkaline peroxide pretreatment on rejects is speculated to have a positive effect on pressroom runnability.



7. The alkaline peroxide pretreatment decreased the air permeability of the rejects pulps.



8. The alkaline peroxide pretreatment increased TEA at a total alkali charge of 5.2%. However, no further improvement was obtained when the total alkali charge increased to 7.4%.



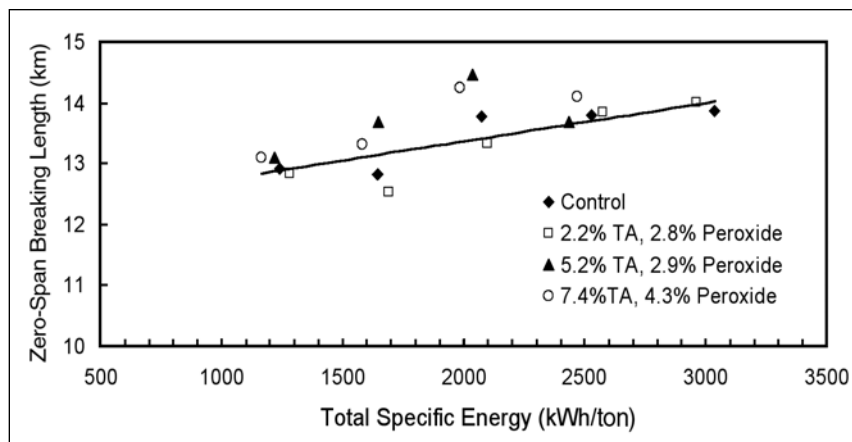
9. The alkaline peroxide pretreatment decreased tear index at a total alkali charge of 5.2% or higher.

At a total alkali charge higher than 2.2%, alkaline peroxide pretreatment decreased light scattering of rejects at a given specific energy as seen in **Fig. 12**. The rejects behave more or less like kraft pulp during refining: the light scattering is lightly decreased at a higher refining energy although more fines were generated at the same time. The decreased

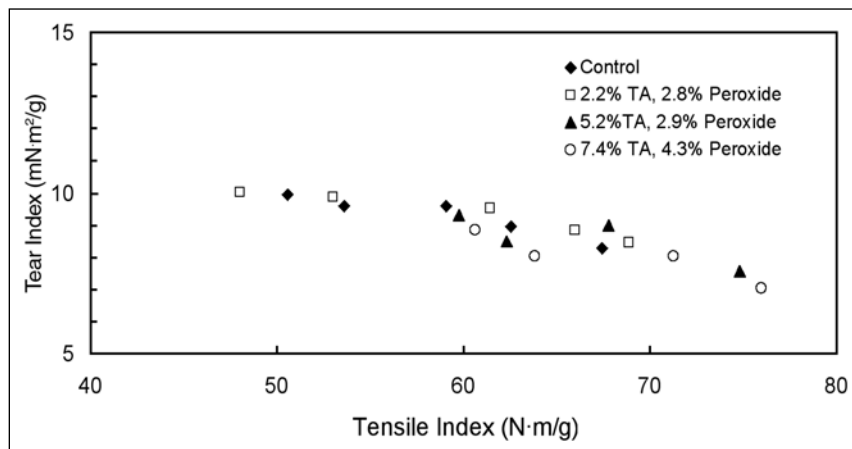
light scattering was due to the reduced bulk as the result of more flexible fibers and increased inter-fiber bonding. As expected, chemical treatments, such as sulfonation, may also decrease light scattering since such a pretreatment would improve inter-fiber bonding as well. Winberg, et al, [5] reported that sulfonation pretreatment of TMP rejects resulted in about 40% loss in light scattering when the pulp sulfonate content reached 1.25%.

Although the light scattering of the rejects was decreased by the alkaline peroxide pretreatment, it is still much higher than that of the softwood kraft pulp, which has a light scattering coefficient of about 20–30 m²/kg. Since alkaline peroxide pretreatment significantly increased the tensile strength of the rejects, it is possible to reduce the reinforcement kraft pulp content in SC and LWC paper. Thus, there is a positive effect on the light scattering coefficient of the final paper. Also, there is a possibility that less calendering could be used to reach the target surface properties since the treated rejects have a low coarseness and are more flexible and conformable. This will help preserve paper light scattering, opacity, and brightness, especially for heavily calendered papers like SC and LWC. Our results on SCA paper supported this and will be reported in Part II of this study.

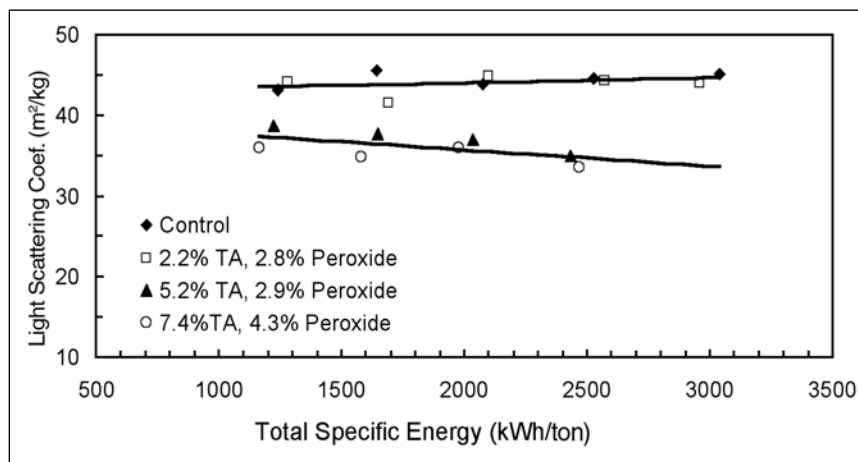
As shown in **Fig. 13**, with the alkaline peroxide pretreatment, the brightness of the pulps was increased from 58.6% to 70%–73% ISO depending on the chemical charges. A 5.2% total alkali and 2.9% peroxide charge gave a brightness of 72%. Note the alkaline peroxide pretreatment conditions have not been optimized yet and also there was no chelation on rejects before the pretreatment. For the control refined rejects, an ISO brightness of 69.4% was obtained using 2.5% total alkali and 1.5% peroxide. Higher brightness is one of the most significant advantages of alkaline peroxide pretreatment over the



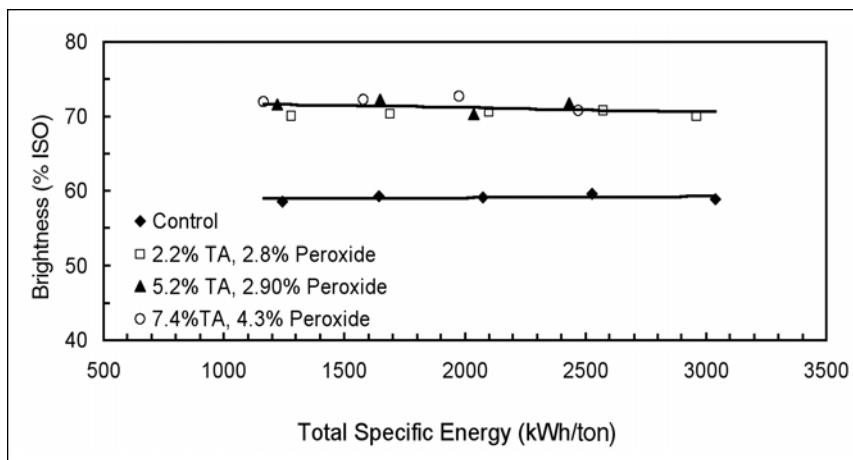
10. Similar or higher zero-span breaking lengths than control were obtained for the refined rejects pretreated with a total alkali charge of 5.2% or higher.



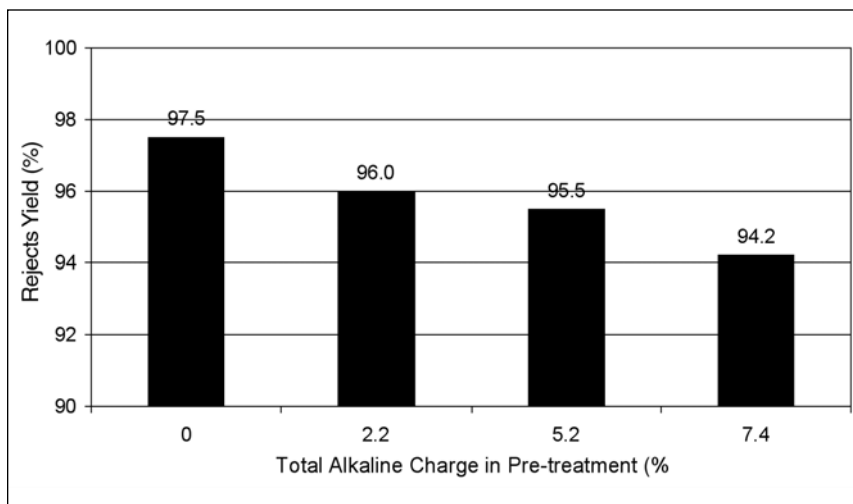
11. Tear index decreased with the increase in tensile index.



12. Alkaline peroxide pretreatment decreased light scattering of the refined rejects at a total alkali charge of 5.2% or higher.



13. Alkaline peroxide pretreatment increased the rejects pulp brightness from 58.6% to 70%-73% depending on the chemical charges.



14. Alkaline peroxide pretreatment decreased rejects pulp yield which is strongly related but not directly proportional to the total alkali charge. Note the control here was the control rejects that were bleached after refining to an ISO brightness of 69.4% with 2.5% total alkali and 1.5% peroxide.

	COD (kg/ton)	BOD (kg/ton)	TOC (kg/ton)	Cationic Demand (μ eq/L)
BLEACHED CONTROL 2.5%TA+1.5% H_2O_2	55.7	20.7	19.5	0.30
2.2%TA,2.8% H_2O_2	56.0	18.4	23.0	0.42
5.2%TA,2.9% H_2O_2	96.5	40.8	30.6	0.51
7.4%TA,4.3% H_2O_2	123.1	96.7	38.0	0.87

II. Effluent characteristics from the alkaline peroxide pretreatment of rejects.

sulfonation process for rejects. For most SC or IWC grades, an ISO brightness of 70%-73% meets its requirement. As a result, there is no need to further bleach the rejects.

Rejects Yield And Effluent Load

As expected, the alkaline peroxide pretreatment resulted in a decreased pulp yield (**Fig. 14**), which is strongly related but not directly proportional to the total alkali charge. This is attributed to the dissolution of organics, such as hemicellulose, extractives, and lignin under the strong alkaline conditions [32-35]. Note the control in Fig. 14 and **Table II** was the control rejects that was peroxide bleached after refining to an ISO brightness of 69.4%. The chemicals used in the bleaching were 2.5% total alkali and 1.5% peroxide.

Corresponding to the yield loss, the effluent load, characterized as COD, BOD, TOC, and cationic demand, was increased at a higher alkali charge (**Table II**). For example, the pretreatment with 5.2% total alkali and 2.9% peroxide increased COD by 73% and also almost doubled the BOD as compared with the control. Again, the data in **Table II** are for the rejects stream only. It should be pointed out that for alkaline peroxide pretreatment, the loss of yield, or the dissolution of organics, was also strongly related to the wood species, temperature, retention time, and peroxide charge [33,34,36].

CONCLUSIONS

Pilot plant trials were conducted to clarify the effect of alkaline peroxide pretreatment on TMP rejects. In general, a 5.2% total alkali seems to be the optimal and 2.2% is not enough to change the freeness-energy relationship. At a total alkali charge of 5.2%, alkaline peroxide pretreatment reduced the specific refining energy by 20% to a given freeness and increased pulp density and tensile strength, most likely as a result of increased fiber flexibility and conformability. The alkaline

peroxide pretreatment had a negligible effect on fiber length and its distribution under the current experimental conditions. Without chelating and washing before refining, refined rejects reached an ISO brightness of 72% with 5.2% total alkali and 2.9% peroxide. A detrimental consequence of the alkaline peroxide pretreatment included reduced light scattering and pulp yield. **TJ**

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INSIGHTS FROM THE AUTHORS

There are a number of studies on sulfonation of rejects [2-7], but very limited reports on alkaline peroxide pretreatment of rejects. Most of the work was reported by Strunk and his colleagues on southern pine TMP and SGW rejects for newsprint [8-11]. No data were available for high value-added mechanical paper grades such as SC and LWC. Compared with newsprint, the mechanical high-value papers have a much higher rejects rate and are usually heavily calendered to achieve target surface properties, therefore, the alkaline peroxide pretreatment on rejects could have a larger impact on these high-value papers.

At a certain total alkali charge, alkaline peroxide pretreatment on TMP rejects not only reduced the specific refining energy by 20% to a given freeness, increased pulp density and tensile strength, but also reduced long fiber coarseness and increased fiber conformability.

For value-added mechanical pulp manufacturers, alkaline peroxide pretreatment on TMP rejects can potentially reduce rejects refining energy, decrease kraft pulp requirement in final paper, and meet increased demand on fiber quality.

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