Impact of Selective Refining Combined with Inter-stage Ozone Treatment on Thermomechanical Pulp

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The aim of this study was to evaluate the performance of selective refining combined with ozone inter-stage treatment in a TMP process. A fractionation process was carried out to separate the primary pulp into two fractions, a long-fibre fraction and a short-fibre fraction. Different charges of ozone, namely 1%, 1.5%, and 2%, were used to treat the long-fibre fraction, and only the treated pulp went to the second refining stage. Finally, the secondary pulp was recombined with the primary short-fibre fraction to be compared to a control TMP trial. Results showed that 21% of the total refining energy can be saved when 1.5% ozone inter-stage treatment is applied before selective refining compared with whole pulp refining, when the pulp freeness is 100 mL. At this level of ozone charge, a slight increase in tensile strength is observed with no significant variation in tear index.

Keywords: Ozone; Fractionation; Selective refining; TMP; Energy reduction; Properties

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INTRODUCTION

Continuous investigation has brought major gains in the mechanical pulping industry regarding reduction of the energy consumption and improvement of pulp and paper quality. However, a more energy efficient pulping process producing better quality pulp and paper is always the major focus for maintaining competitiveness despite the continuous increase of manufacturing costs, including fibrous materials and energy costs. The refined pulp can be divided into three parts: long (> R48) fibres, short fibres (R100+R200), and fines (P200). In mechanical pulping, long fibres create the main fibre network during the papermaking process; thus, the main mechanical resistance of the sheet is determined by the long fibres. For primary pulp, long fibres present three quarters of the whole pulp. It has been shown that long fibres possess poor inter-bonding ability compared with short fibres and fines (Law 2005). Thus, it is very interesting to develop the bonding abilities of long fibres and at the same time increase their flexibility. Law (2005) indicates that it is difficult to enhance fibre bonding if one relies only on selective refining of long fibres without chemical modification. Therefore, a chemical treatment is needed to modify the long fibres prior to the secondary refining.

For mechanical pulp fibres, one of the main reasons for low inter-fibre bonding is the presence of lignin, although the hydrophobic lignin needs to be retained to give the high yield and high bulk property to mechanical pulp (Li *et al*. 2010). Applying a chemical agent to modify the lignin-rich material on the fibre surface can improve the bonding ability of mechanical pulp fibres while maintaining the high yield. Ozone is known to be a powerful oxidizing agent that has already been used in industrial pulp bleaching (Germer *et al.* 2011; Cloutier *et al.* 2009; Cloutier *et al.* 2010). Ozone has been found to have a positive effect on both energy savings (Lecourt *et al*. 2007; Petit-Conil 2003) and on pulp qualities (Katz and Scallan 1983).

In our previous study (Sun *et al.* 2013), it was found that the presence of sodium hydroxide is important in the ozone treatment of mechanical pulp. Ozone has a good performance when the reaction pH is between 5.4 and 6.15 and the reaction is carried out with whole primary pulp. Short fibres and fines have much larger specific surfaces and more contact with chemical components than do long fibres (Han *et al*. 2008). In this study, a two-stage fractionation process using a screen basket with very small apertures was employed to separate the primary pulp into two fractions. This fractionation process is based on fibre length, and it has been shown to be an efficient way to separate primary pulp by our research group (Ferluc 2008). To compare with the previous study of ozone performance in mechanical pulp, only long fibres of primary pulp were treated with ozone before proceeding to the secondary refining. Then, the primary short-fibre fraction was recombined with the secondary pulp to evaluate the feasibility of selective refining with or without chemical treatment. More information about fiber morphology can be found in Sun *et al.* 2014.

EXPERIMENTAL

Materials

The pulp used for ozone treatment was recovered after the first stage refining of the thermomechanical pulping process from the Kruger mill located in Trois-Rivières, Québec. This primary pulp, made from mixed chips of spruce and fir, had a freeness of 565 mL with a specific energy consumption of about 6.5 MJ/kg.

Fractionation

The primary TMP was fractionated into two fractions before ozone treatment: a long-fibre fraction (> R48) and a short-fibre fraction (P48). This fractionation process has been proven to be efficient by Ferluc *et al.* (2008). This process is based on fibre length, using a 0.25-mm smooth hole basket. In this two-stage fractionation process, 13.7% of the short fibres of the total pulp is extracted in the first stage and another 6.2% is separated during the second stage.

Ozone Treatment

An Ozonia OZAT unit (Degrémont Ltée, Dorval, Qc, Canada) was used to produce the ozone from oxygen to produce a gas mixture containing 10% by weight of ozone. The primary long-fibre fraction was treated with different charges of ozone, *i.e.*, 1%, 1.5%, and 2%, respectively. Before injecting ozone gas into the reactor, sodium hydroxide solution was added to adjust the reaction pH number. After treatment with ozone, the pulp pH was about 5 for each trial containing ozone inter-treatment. For each trial, the pulp quantity was about 20 kg and the consistency was 30%. All the treatments were done at 85 °C and for 15 min.

Refining

The pulps (20 kg, 30% consistency) were diluted with water after ozone treatment to obtain 20% consistency prior to the second refining stage. The second refining stage was realised at the Lignocellulosic Material Research Centre, LMRC (Trois-Rivières, QC, Canada), using a Metso CD 300 pilot refiner under atmospheric conditions. The refiner plate gap was adjusted during a single-pass refining process to obtain pulps with different freeness levels. At the end of the secondary refining stage, the pulps reached temperatures of 90 to 95 °C.

Pulp and Paper Properties

Pulp properties were evaluated on 60 g/m^2 handsheets prepared with a British sheet-mould former according to PAPTAC method C.4. Scott internal bond strength was measured according to TAPPI T833. Handsheet physical properties were measured according to PAPTAC methods D.34, D.9, and D.8. The optical instrument Color Touch PC (Technidyne Corp., USA) was used to measure the optical properties of the handsheets. The brightness and opacity were determined using PAPTAC methods E.1 and E.2. The light scattering coefficient and the light absorption coefficient were measured using TAPPI method T1214. All graphics were produced with Excel software (Microsoft), with the default curve fitting adapted to the tendency (linear, log, or power fitting).

RESULTS AND DISCUSSION

Refining Energy

Energy consumption is an important factor for thermomechanical pulping because high energy is always demanded and it takes around 15 to 30% of the production cost, affecting the profitability of this type of pulp. Fig. shows the specific energy consumption of secondary refining of long fibres, treated or not treated with ozone, as a function of pulp freeness. Selective refining of long fibres had a positive effect on energy savings. During fractionation, 80.1% of the whole fibres were retained, and all of these fibres were treated or not treated with ozone before they further underwent secondary refining. After that, the short-fibre fraction was recombined with the secondary pulp. The removal of about 20% of fibres by fractionation and selective refining (mainly fines and short fibres), without ozone treatment, led to about 28% less energy consumption during the secondary refining stage, equal to 15% of total refining energy at 100 mL pulp freeness. This means selective refining of long fibres can lead to less energy wastage.

Ozone treatment can also give significant energy savings, as shown in Fig.. Cellulose and lignin are the two most important wood components affecting the energy consumption during the refining process. A study has shown that the lignin oxidation rate with ozone is much faster than cellulose decomposition (Arias *et al*. 1997). Hence, it can be concluded that the reduction of energy consumption from ozone treatment is primarily from the modification of lignin. In this research, ozone was applied to the long-fibre fraction of primary pulp. With 2% ozone, about 23% of the secondary refining energy (9% on total refining energy) could be saved compared with selective refining without ozone treatment when the pulp freeness is 100 mL. Compared with control TMP refining, the energy reduction was about 44% (23% on total refining energy) under the same conditions. In our previous study, when 2% ozone was applied to a whole primary pulp under the same pH condition, about a 26% reduction in secondary refining energy was gained compared to a normal TMP trial when the pulp freeness was 100 mL. This means that ozone more easily reacts with the short fibres or fines than with the long fibres, primarily because the specific surface areas of the short fibres and fines are much larger than that of long fibres (Han *et al*. 2008). However, ozone still has a good effect on the results of long fibre refining.

The difference in energy consumption is not large when producing a pulp of 100 mL when the ozone charge is between 1.5% and 2%. Therefore, the properties of pulp and paper need to be discussed to determine the most suitable ozone charge.

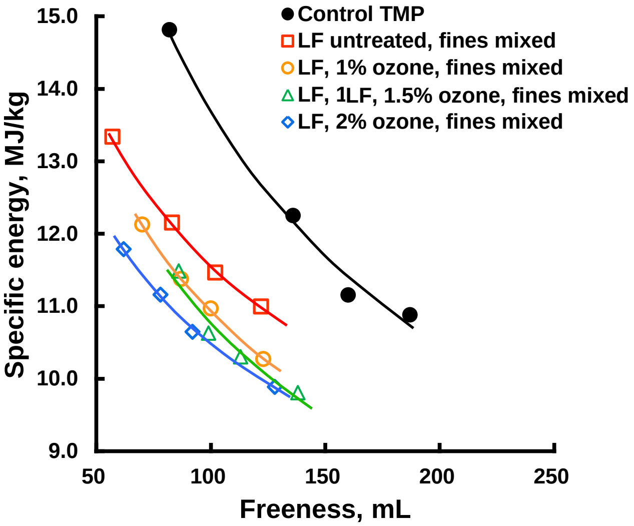


Fig. 1. Pulp freeness *versus* specific energy consumption (LF: refined Long Fibre fraction)

Fibre Distribution

Fig. shows the fibre distribution of long fibres after secondary refining with or without ozone treatment compared with a control TMP trial as a function of freeness. The fibre distribution of secondary fibres varies when long fibres of the primary pulp are treated with different charges of ozone. With 1 to 1.5% ozone applied, the secondary pulps contain much more R14+R28 fractions compared with selective secondary refining of the long-fibre fraction untreated by ozone. This could be explained by ozone, which reacts mainly with the lignin at the fibre surface to form more carboxylic acid groups (Chang *et al*. 2012; Katz and Scallan 1983; Zhang *et al*. 1997). This can make the fibres more flexible and swollen mainly by changing the lignin-rich surface of the fiber, since the ozone only slightly penetrates the wall structure; these changes enhance the fibre development during secondary refining.

When 1.5% ozone was charged, the R14 fraction of secondary fibres remained unchanged with a decrease in freeness. This indicates that at this level of ozone treatment, long fibres had been developed more during the refining process instead of being collapsed or cut. To support this point, a better inter-fibre bonding strength was observed under this ozone treatment condition; the fibre bonding strength will be discussed later in this paper. However, when the ozone charge was up to 2%, the R14 fraction of the secondary pulp decreased to a lower level and R28 remained at a similar level compared to other charges of ozone. This means that with 2% ozone, the intrinsic fibre strength was affected. Ozone had no significant effect on the generation of short fibres. With the short-fibre fraction of primary pulp recombined into the secondary pulp, the short fibre proportion would be slightly higher compared with the control TMP trial. For the recombined pulp with ozone treatment, the amount of R14+R28 fibres was higher than it was for the control TMP.

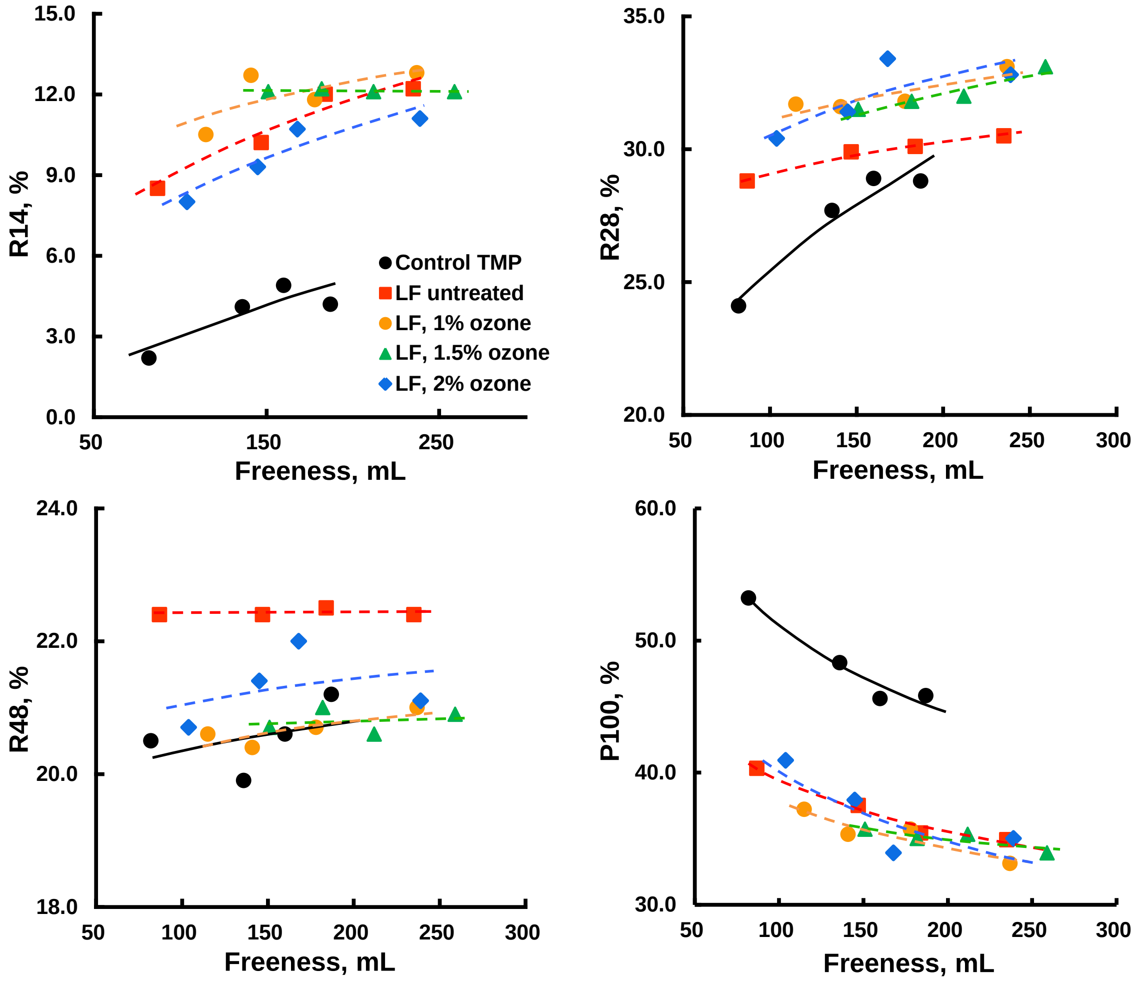


Fig. 2. Fibre distribution of secondary pulp with or without ozone treatment

Physical and Optical Properties

Scott bond is used to evaluate the internal bonding strength, which plays an important role in paper qualities. Inter-fibre bonding strength has an effect on other essential physical properties, including the tensile index and tear index. Bonding strength can be influenced by the species of raw materials, the refining process, and also the chemical treatment during the process (Koubaa and Koran 1995). It is evident that a better inter-fibre bonding strength can be gained with ozone inter-stage treatment. Especially with 1.5% ozone applied, when pulp freeness becomes lower than 150 mL, the bonding strength is developed faster than for higher freeness compared with 2% ozone addition.

When the primary short-fibre fraction was recombined with the secondary pulp, either treated or not treated with ozone, in proportion to reform the initial pulp, the fibre bonding strength of these handsheets did not show an advantage compared with control TMP (Fig. 3). This means the primary short fibres and fines contribute less to ameliorate the inter-fibre bonding ability compared with primary long fibres being developed during the second refining stage. In mechanical pulp, the primary short fibres and fines principally come from the middle lamella and primary fibre wall, so they are more flake-like rather than fibril, which results in less fibre bonding and so less tensile strength (Luukko 1999).

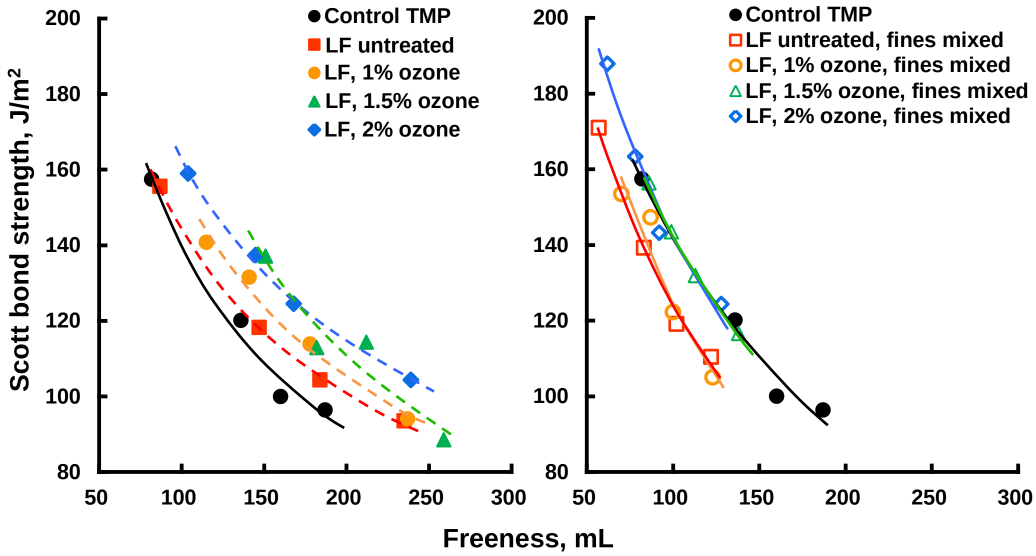


Fig. 3. Inter-fibre bonding strength as a function of freeness

The tensile and tear indices are two important indicators to evaluate paper properties that are directly influenced by the fibre performance during the refining process. Both of these indexes are determined synthetically by several elements, for example, fibre strength and fibres' inter-bonding abilities. As has been discussed above, selective refining of primary long fibres can maintain more long fibres, especially when 1 to 1.5% ozone is applied as an inter-stage treatment. This could have a positive effect on both of the indexes, as a long fibre can have much more inter-bonding with other fibres than can a short fibre.

As shown in Fig., selective refining of the primary long-fibre fraction without ozone treatment can augment the tensile strength without disturbing the tear index compared with the control TMP. The recombined pulp of selective refining without ozone treatment exhibited about a 15% better tensile strength, with the same tear index, compared with control TMP.

Ozone seems to have had a negative effect on the tear index. Handsheets made with the secondary long fibres with ozone treatment, without adding primary short fibres, showed decreased tear strength, especially when accompanied with increased ozone charge. This indicates that with the amelioration of inter-fibre bonding ability, the fibre itself becomes weakened; similar results have been published (Chang *et al*. 2012; Lindholm 1977). Another possible reason for this result is that ozone reacts with the lignin at the fibre surface; one of the functions of lignin is to make the fibre stiff. Because of the modification of lignin during the ozone reaction, the fibre is less stiff and fibres are more easily broken down during the tear test. However, when the primary short-fibre fraction is remixed into the secondary pulp, the decrease in the tear index is not significant; a change could be observed only when 2% ozone was applied. The contribution of short fibres and fines will be discussed in another paper that focuses on the fibre characteristics during selective refining with ozone treatment.

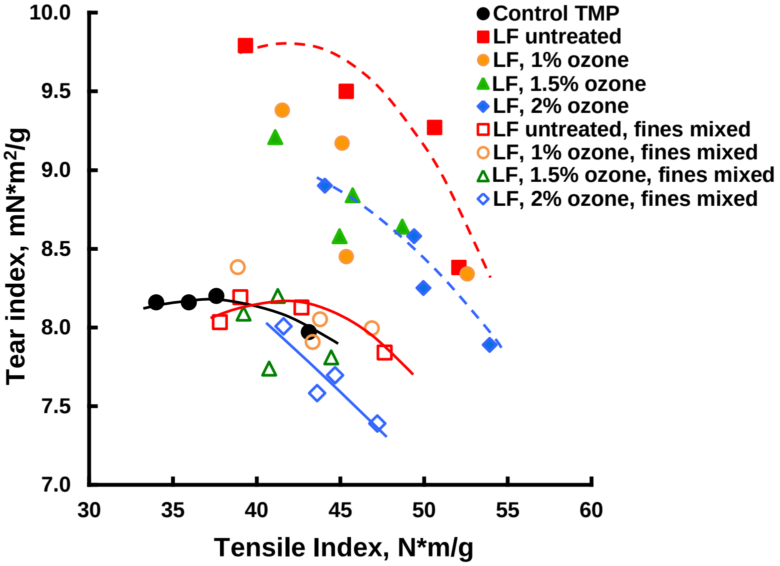
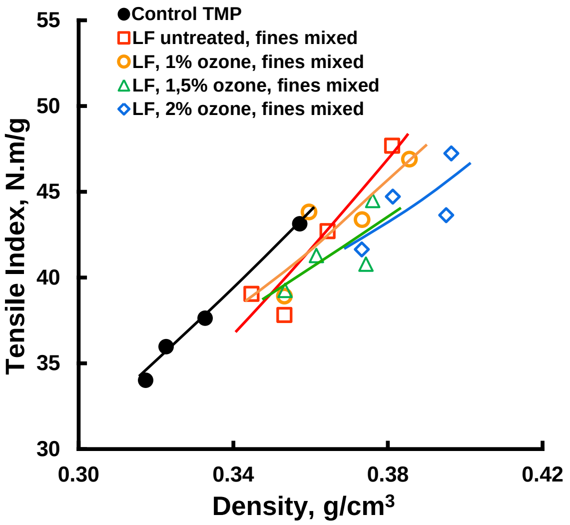


Fig. 4. Correlation between tensile index and tear index

In this research, the tensile strength of all the samples increased almost linearly with increasing handsheet density, as shown in

Fig.. However, the slope of the trend line of each trial was different. This means that the mechanism of tensile development was changed when fractionation and ozone inter-stage treatment were applied. With the same handsheet density, selective refined pulps without ozone treatment or treated with lower ozone charge provided a higher tensile strength. This is possibly because when the sheet density increases, individual fibre strength plays a more important role in governing paper tensile strength (Vena 2005), and the ozone reaction leads to weakened fibres.



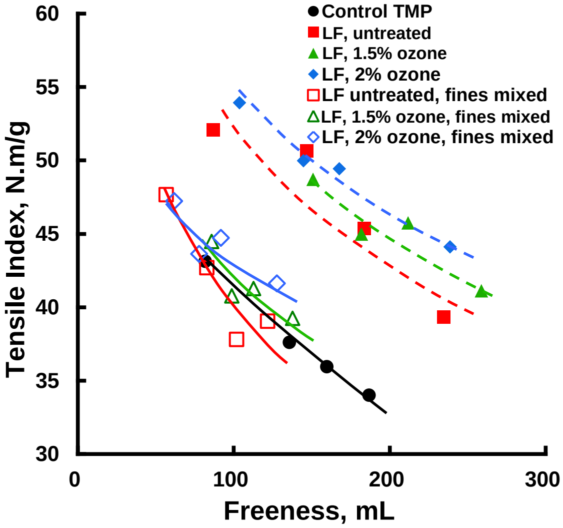


Fig. 5. Correlation between tensile strength and sheet density

Fig. 6. Correlation between tensile strength and pulp freeness

An improvement of tensile strength could be observed when long fibres were treated with 1.5% ozone without being remixed with primary short fibres after secondary refining compared with no ozone treatment, as shown in Fig. 6. However, this improvement would be lost when the secondary pulp is recombined with primary short fibres. The primary fines and short fibres are lignin-rich components, with poor bonding ability. With the joining of these flake-like primary fines, a significant decrease in tensile strength was observed. The reconstructed pulps treated with ozone still had a better tensile strength, even with the negative effect of adding primary fines and short fibres, compared with control TMP.

In this study, the light scattering coefficient of the handsheet increased with the development of tensile strength for each trial, as shown in Fig. 7. This can be understood as being due to the generation of more fibre inter-bonding area and fines as a result of developing tensile strength. Both of these modifications contributed to a higher light scattering coefficient. However, ozone seems to have had a negative influence on the light scattering coefficient compared with when only selective refining was done. The modification of fibre surface and generation of more carboxyl acid groups during ozone inter-stage treatment can lead to fewer fines and short fibres. Additionally, ozone reaction with fibres can affect the mechanisms of fibre development and rupture during further refining. After treatment with ozone, fibre collapse and peeling-off occurs more from the secondary wall instead of at the interface of the primary wall and middle lamella. As a result, more fibrillar elements are produced, which contribute more to tensile strength and less to light scattering than flake-like particles (Luukko 1999). These may be the two main reasons that light scattering coefficient is reduced when different charges of ozone are applied to the primary long fibres.

Another important observation is that when secondary pulp was recombined with the primary short-fibre fraction, the light scattering coefficient increased more quickly with ozone inter-treatment compared with selective refining without ozone. Thus, the undesired influence of ozone on the light scattering coefficient can be balanced at lower pulp freenesses. The decrease of the light scattering coefficient was quite slight when 1.5% ozone was applied compared to the control TMP.

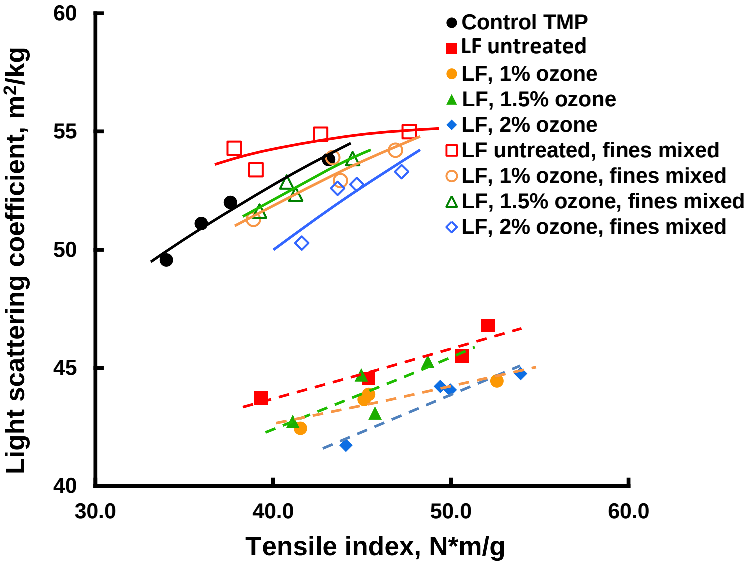


Fig. 7. Correlation between the light scattering coefficient and tensile index

A decrease in handsheet brightness could be observed with a slight increase in paper opacity when inter-stage ozone treatment was applied under different ozone charge levels, as can be seen in Fig. 8. The highest brightness drop was observed when 2% ozone was applied, and the brightness loss was about 5 units compared with long fibre refining without ozone treatment. When increasing ozone charge was applied, brightness did not vary significantly, with a difference within 1 unit. An improvement of brightness was observed by recombining the secondary pulp with primary short fibres and fines. Handsheet opacity was also enhanced; an increase of 2 units can be gained for each level of ozone charge when the pulp freeness is 100 mL. Among different ozone charges, a small increase of opacity was observed with the augmentation of ozone charge. This may be due to the contribution of paper density, as with higher density, higher opacity can be obtained (Vena 2005).

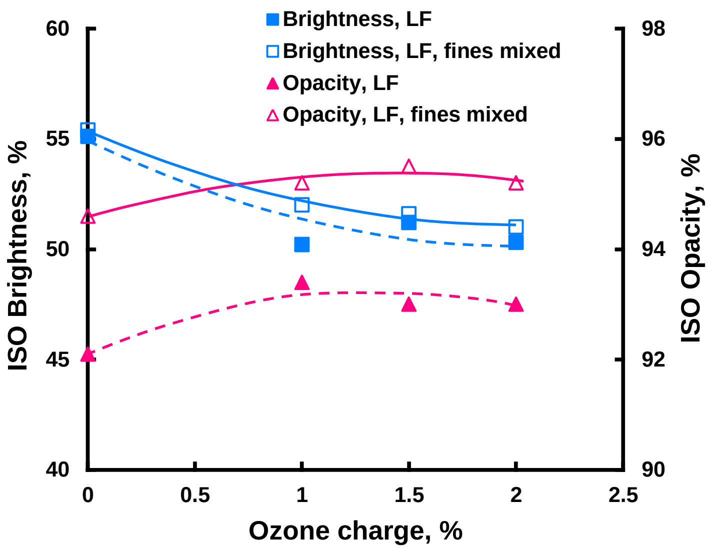


Fig. 8. Effects of ozone at different charges on handsheet brightness and opacity with pulp freeness of 100 mL

CONCLUSIONS

1. The effect of selective refining of the primary long-fibre fraction combined with an inter-stage ozone treatment on energy consumption and pulp qualities has been studied. Secondary pulp was recombined with the primary short-fibre fraction to form the initial pulp for comparison with a traditional TMP process. Selective refining shows a huge advantage with respect to refining energy; about 15% total refining energy could be saved when obtaining a pulp of 100 mL freeness, compared with the control TMP trial. Additionally, with 1.5% ozone applied, another 13.8% energy savings can be attained.

2. Selective refining does not greatly change the physical properties of the handsheet, and an increase of the light scattering coefficient can be observed.

3. Ozone treatment with primary long fibres can modify the secondary pulp properties compared with selective refining only. However, this improvement could disappear when secondary pulp is recombined with primary short fibres. This is primarily because of the poor bonding ability of the primary fines.

4. The same phenomenon does not exist for the optical properties. Recombining long fibres and fines results in an augmentation of the handsheet brightness, opacity, and light scattering coefficient.

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