Investigation of ESEM/EDX to measure liquor penetration and diffusion in *Eucalyptus grandis* wood chips during kraft pulping

Valerie Grzeskowiak[1], Asheena Hanuman[2] and Jerome Andrew[2]*

[1]Sappi Technology Centre
[2]CSIR Natural Resources and the Environment – Forestry and Forest Products (FFP) Research Centre
Corresponding author: jandrew@csir.co.za

ABSTRACT

Environmental scanning electron microscopy coupled with energy dispersive x-ray (ESEM/EDX) was optimised to measure the penetration and diffusion of cooking liquor into Eucalyptus grandis wood chips during kraft pulping. The moisture content of the cooked wood chips influenced the ESEM/EDX measurement of sodium and sulphur, whilst the contribution of sodium and sulphur already present in the wood prior to pulping was negligible. Using the optimised ESEM/EDX method, investigations into the use of pulping aids during kraft pulping showed that the penetration and diffusion of sodium and sulphur was enhanced by the use of anthraquinone (AQ) and a combination of AQ and surfactant. As expected, chip thickness was found to influence the penetration and diffusion of cooking liquor into the wood structure during cooking.

1. INTRODUCTION

The kraft pulping process is one of two predominant chemical pulping processes used in the pulp and paper industry [1]. During this process, delignification occurs when lignin from the wood is degraded and removed with the cooking liquor. The cooking liquor consists of a solution of sodium hydroxide and sodium sulphide. Uniform distribution of cooking liquor throughout the wood chips results in uniform delignification which in turn produces high yield and high quality pulps [2]. The distribution of liquor within the wood structure occurs in two stages [3]. The first stage is penetration of liquor where the cooking liquor flows into the air filled voids of the wood chips under a pressure gradient. This is followed by the second stage where the ions and other soluble matter in the liquor diffuse through the wood chips under a concentration gradient. Liquor penetration and diffusion is affected by chip dimensions (length, width and thickness), with chip thickness being the most critical [4]. It can be enhanced through the use of pulping additives such as anthraquinone (AQ) and surfactants. Anthraquinone increases delignification and protects the carbohydrates from the peeling reaction. Surfactants wet and emulsify the extractives in the wood chips and are able to keep the lignin and extractives in solution [5]. These pulping additives are effective in small quantities and reduce cooking time, kappa number, alkali

consumption, cooking temperature and rejects. In addition, they also improve pulp washing, pulp viscosity and yield [5, 6].

There are currently several methods documented in the literature to measure liquor penetration and diffusion [4, 7–13], but no standard method exists. The South African pulp and paper industry expressed their need for a simple and reliable measurement method that, in turn, will facilitate a better understanding of factors affecting liquor penetration and diffusion. A review of the literature has shown that Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX) can be used as a method to measure liquor penetration and diffusion in wood chips [8]. The advantage of this method is that it is able to qualitatively show the profile of the ions in the liquor as the ions travel from the edge of the wood chip towards the centre, as well as quantitatively show the amount of ions that have impregnated the wood chip after penetration and diffusion. In this study, Environmental Scanning Electron Microscopy/Energy Dispersive X-ray (ESEM/EDX) was used owing to the added advantage of the technique being non-destructive and simpler to use. A major advantage of ESEM/EDX over SEM/EDX is that it can be used for non-conductive samples without the need for carbon coating the sample to increase its conductivity. This eliminates the interference of carbon from the analysis [14].

The objective of this study was two-fold. The first objective was to optimise the ESEM/EDX method for measurement of liquor penetration and diffusion in wood chips. This was achieved by investigating factors that affect ESEM/EDX measurement such as moisture content and interference of sodium and sulphur already present in the uncooked wood chips. Subsequent to this, the sensitivity and repeatability of the method was assessed. The second objective was to then use the optimised ESEM/EDX method to illustrate its applicability by measuring the influence of pulping aids and chip dimensions on liquor penetration and diffusion during kraft pulping.

2. MATERIALS AND METHODS

2.1 Sampling

Five ten-year-old *Eucalyptus grandis* trees were sampled from a single compartment. From each tree, a 1.3m bottom billet was taken, debarked and

cut into disks measuring 3cm in thickness. Cubes measuring 3cm x 3cm x 3cm were then cut along the diameter of each disk. The remaining parts of the disk were chipped into 25mm lengths using a laboratory guillotine chipper (see Figure 1).

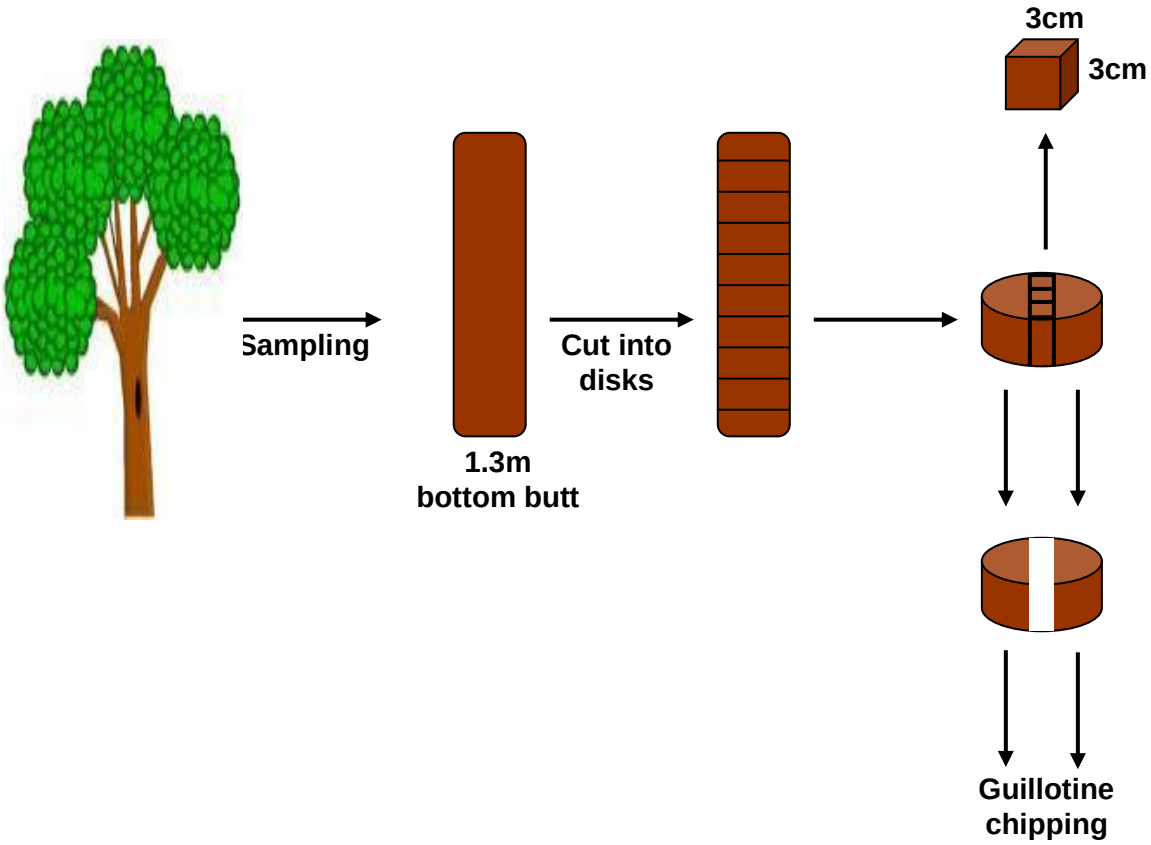

Figure 1. Sampling and sample preparation for kraft pulping.

2.2 Pulping

Pulping was carried out in electrically heated rotating digesters using the kraft process. Eight hundred grams oven-dry equivalent chips per cook were pulped using the conditions summarised in Table 1**.** During pulping, the moisture content of the chips was taken into account in order to maintain a constant liquor-to-wood ratio. A typical pulping cycle entailed ramping the digester temperature from ambient (~25°C) to 170°C at a rate of 1.6°C/min.

The optimisation of ESEM/EDX measurement was carried out on kraft cooks that were terminated at 70mins and 110mins into the cooking cycle.

To determine the influence of chip dimensions on liquor penetration and diffusion, kraft cooks were stopped at 60mins into the cooking cycle.

Wood cubes with dimensions 3cmx3cmx3cm was used to study the influence of pulping additives on penetration and diffusion. For this purpose, three wood cubes were added to the wood chips prior to kraft pulping. A total of four cooks were carried out according to Table 2. Cooks were dosed with either 0.05% AQ, 0.28% surfactant or a combination of both. The dosages were calculated on an oven dry chip basis.

Table 1: Pulping conditions for the different kraft cooks.

	Influence of chip dimensions and pulping aids	**Optimisation of ESEM/EDX**
Mass of chips pulped (oven dry equivalent)	800g	800g
Sulphidity (as Na_2S)	25%	25%
Active alkali (as Na_2O)/oven dry chips	18%	18%
Liquor-to-wood ratio	4.5:1	4.5: 1
Heating rate to maximum temperature (170°C)	1.61°C/min	1.61°C/min
Pulping time	Stopped after 60mins heating	Cook 1 - stopped after 70mins heating Cook 2 - stopped after 110mins heating

Table 2: Composition of the different kraft cooks.

Cook 1	**Cook 2**	**Cook 3**	**Cook 4**
Control	AQ (0.05%)	Surfactant (0.28%)	AQ (0.05%) + Surfactant (0.28%)

In most instances the wood chips were partially cooked due to the short cooking times. This was intentional so as to only partially impregnate the

chips with cooking liquor. After cooking, the black liquor was removed from the partially cooked wood chips by dumping the chips onto a 10 mesh screen to allow the black liquor to drain. After 10mins, the chips were pat dry with paper towels to remove excess black liquor from the surface of the chips. The chips were then placed into plastic bags, sealed and frozen at -4°C until required.

2.3 ESEM/EDX instrument settings

The instrument used was a Philips XL30 ESEM with EDAX detector and XL SEM and EDX control software. Analysis was carried out in low vacuum mode on uncoated wood chips. The instrument settings are shown in Table 3. Elements measured included C, O, Na, Mg, Al, Si, P, S, Cl, K and Ca, and were expressed as atomic %.

Table 3: ESEM/EDX instrument settings to measure liquor penetration and diffusion.

Magnification	65x
Accelerating voltage	15 kV
Working distance	9–12 mm
Counts per second	1500–2500 cps
Measurement window	1x1 mm

Sample preparation

Each wood chip was cut in half and was measured from top to bottom along the direction of the fibre at 1mm intervals (see Figure 2).

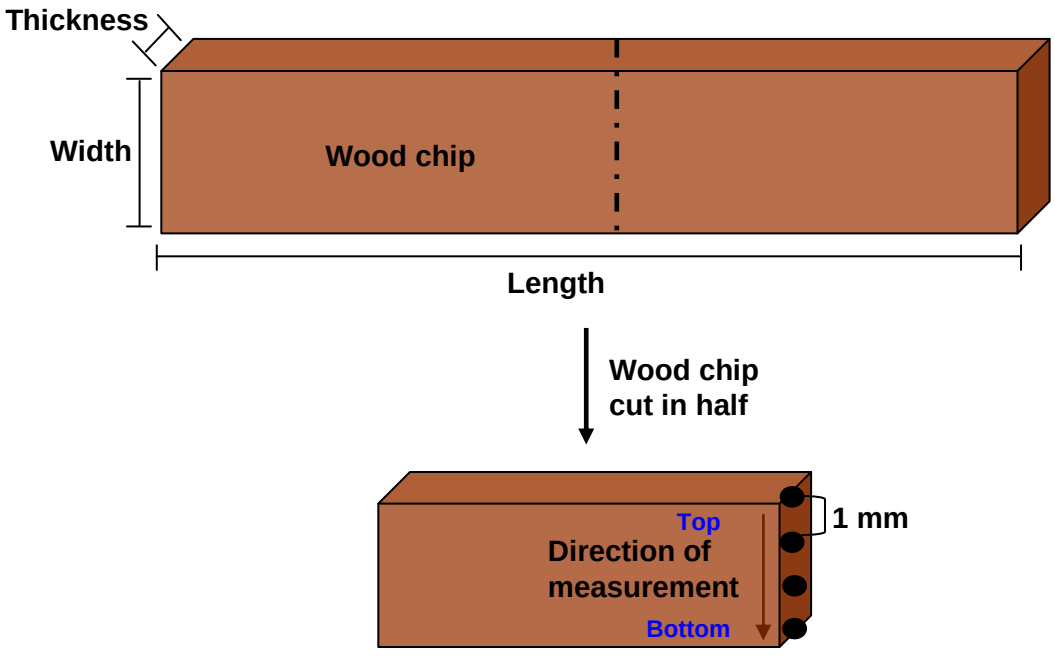

Figure 2. Direction of ESEM/EDX measurement of wood chips

2.4 Optimisation of ESEM/EDX

2.4.1 Repeatability

A wood chip was sampled from each cook stopped at 70mins and 110mins. The sodium and sulphur content was measured using ESEM/EDX. Each chip was measured 5 times at the same position in the chip.

2.4.2 Sensitivity

Three wood chips of similar dimensions were sampled from the 70mins and 110mins cooks and the sodium and sulphur content was measured using ESEM/EDX.

2.4.3 Impact of moisture on ESEM/EDX measurement

The impact of moisture content on ESEM/EDX measurement was assessed by using three cooked wood chips from the 70mins cook. Each chip was cut in half. The first half was dried in an oven at 110˚C overnight before being measured with ESEM/EDX. The second half of the chip was measured directly from the cook with no prior drying (Figure 3).

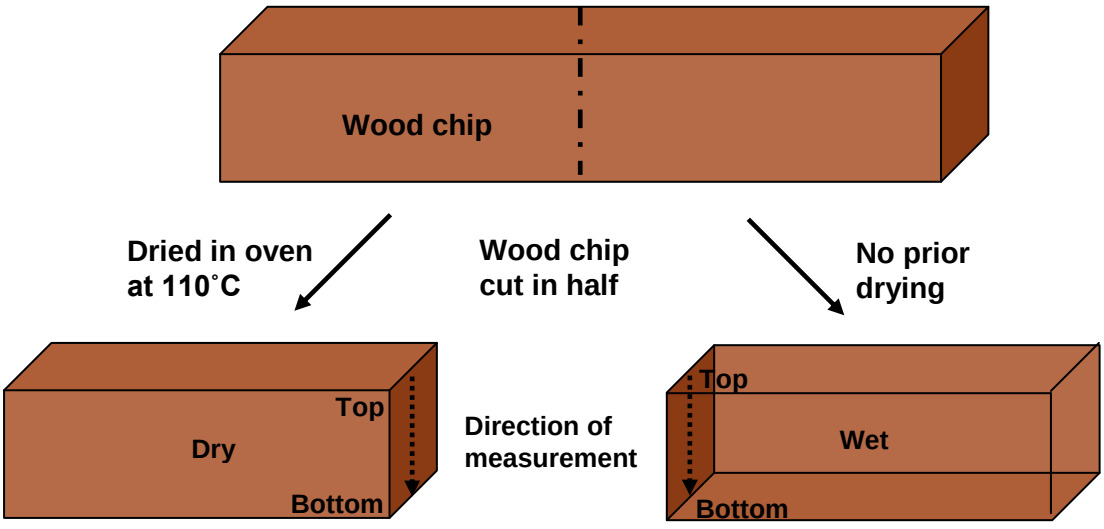

Figure 3. Sample preparation and measurement of wood chip for ESEM/EDX analysis to determine the impact of moisture.

2.4.4 Contribution of sodium and sulphur from uncooked wood to ESEM/EDX measurements

Three uncooked and three cooked chips were measured with ESEM/EDX to assess the contribution of sodium and sulphur from the uncooked wood.

2.5 Influence of chip dimension and pulping aids

Cubes from each 60mins cook (shown in Table 2) were oven dried at 110ºC overnight and then measured to determine the influence of pulping additives on liquor penetration and diffusion. Chips of similar width and length but different thickness (4mm and 6mm) were analysed from each cook to determine the influence of chip thickness on liquor penetration and diffusion.

3. RESULTS AND DISCUSSIONS

3.1 Optimisation of ESEM/EDX analysis

3.1.1 Influence of chip moisture content on sodium and sulphur measurement

The moisture content of chips influenced the measurement of sodium and sulphur using ESEM/EDX. Dry chips showed approximately three times higher amounts of both elements compared to never dried chips (Figures 4 and 5). A possible explanation for this could be due to the concentration of oxygen being higher in the never dried chips due to its contribution from water. Since each elemental percentage is calculated from the total elemental composition, an increase in oxygen concentration could result in a decrease in the concentration of the remaining elements. Based on this finding, subsequent chip samples were oven-dried at 105°C to constant weight prior to measurement by ESEM/EDX.

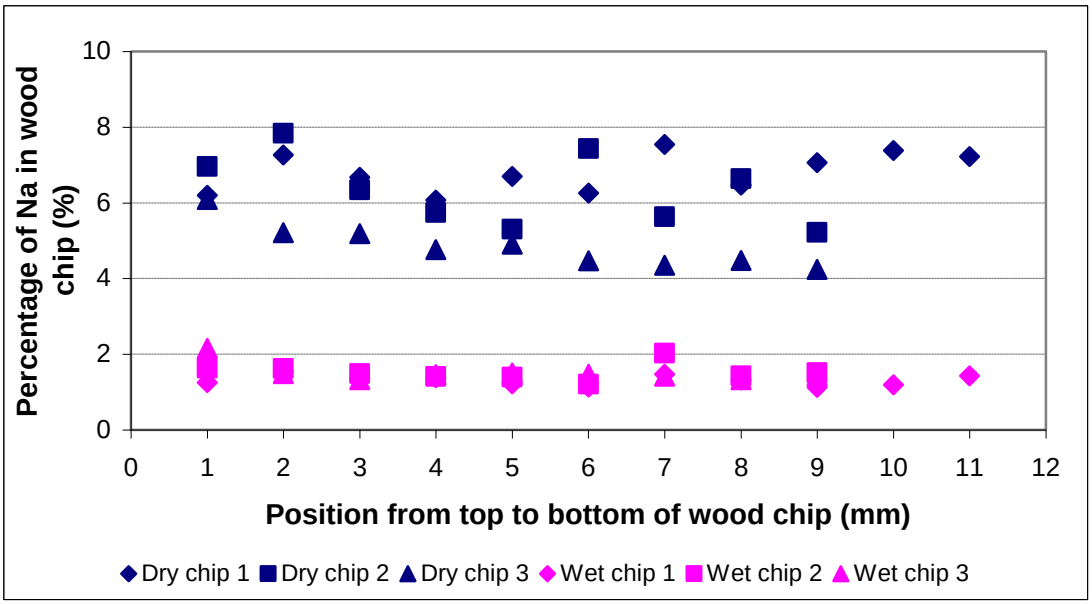

Figure 4. Percentage of sodium in dry and wet chips measured with ESEM/EDX.

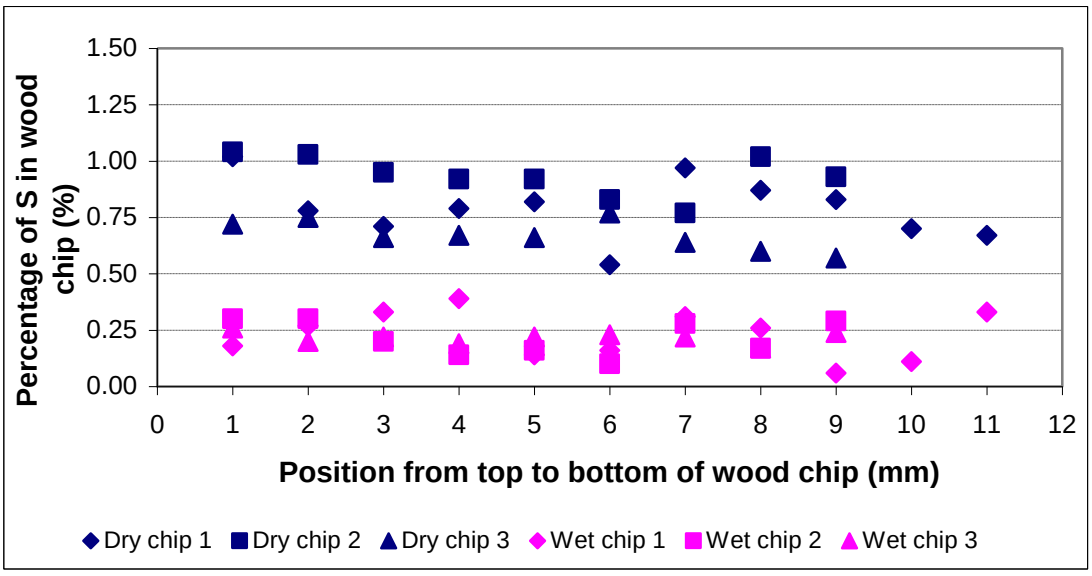

Figure 5. Percentage of sulphur in dry and wet chips measured with ESEM/EDX.

3.1.2 Contribution of sodium and sulphur from uncooked wood chips

Due to the low amounts of sodium and sulphur measured in the cooked wood chips, it was important to establish the baseline concentration of these elements present in the uncooked wood and its subsequent impact on ESEM/EDX measurements. For this purpose, three uncooked chips were measured using ESEM/EDX and were compared to measurements carried out on cooked wood chips. The results showed that the average sodium and

sulphur content in the uncooked wood was around 0.16% and 0.04%, respectively, and appeared to be sufficiently low, compared to the cooked wood chips, to not influence the ESEM/EDX measurements. The sodium and sulphur content in the cooked wood chips averaged around 2.5% and 0.3%, respectively (Figures 6 and 7).

Figure 6. Comparison of sodium content in uncooked and kraft cooked wood chips.

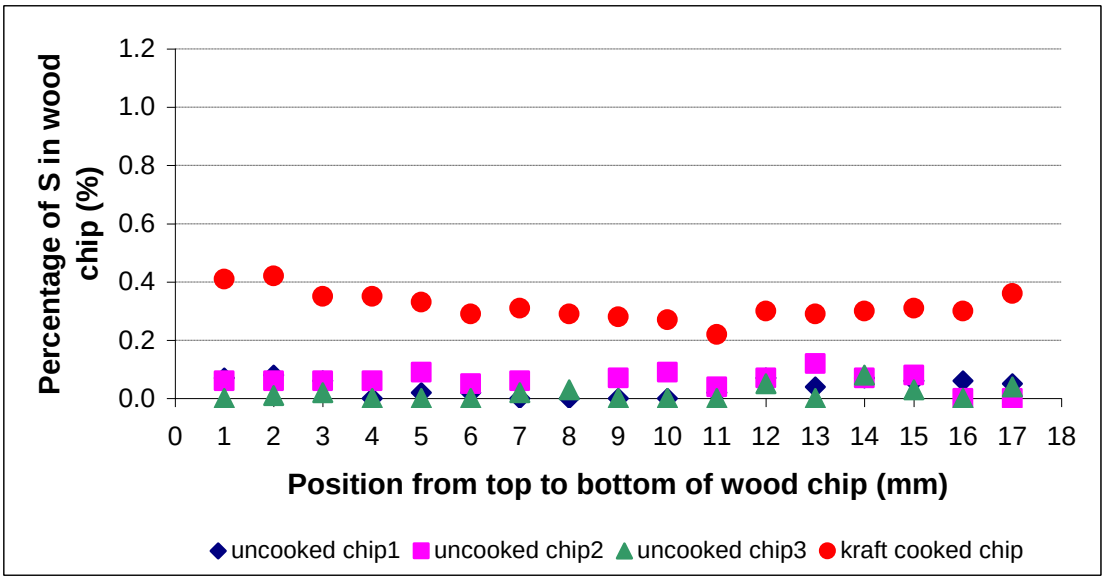

Figure 7. Comparison of sulphur content in uncooked and kraft cooked wood chips.

3.1.3 Sensitivity of the ESEM/EDX measurement

The low concentrations of sulphur and sodium present in the cooked wood chips also raised concerns about the sensitivity of the ESEM/EDX method to detect changes in the concentration of these elements during different cooking regimes. In order to address this, the sodium and sulphur profiles were measured on chips cooked for different periods of time. The hypothesis was that the longer the cooking times of the chips, the greater the penetration and diffusion of cooking liquor in the chips, and hence a greater concentration of sodium and sulphur present in the chips. The intention was to determine if the ESEM/EDX method was sensitive enough to detect these changes in concentration for different cooking periods. Figures 8 and 9 show the sodium and sulphur content of chips cooked at 70mins and 110mins. As expected, the results showed that the wood chips cooked for longer had a higher concentration of sodium and sulphur compared to the wood chips cooked for a shorter period of time. In addition, the results in Figures 8 and 9 also show that the concentration of Na and S decreased towards the centre of the chip. This was because there was insufficient time for uniform diffusion of liquor into the centre of the wood chips for the shorter cooks. This was less pronounced for the 110mins cook due to the longer time available for diffusion of the cooking liqour into the centre of the chips.

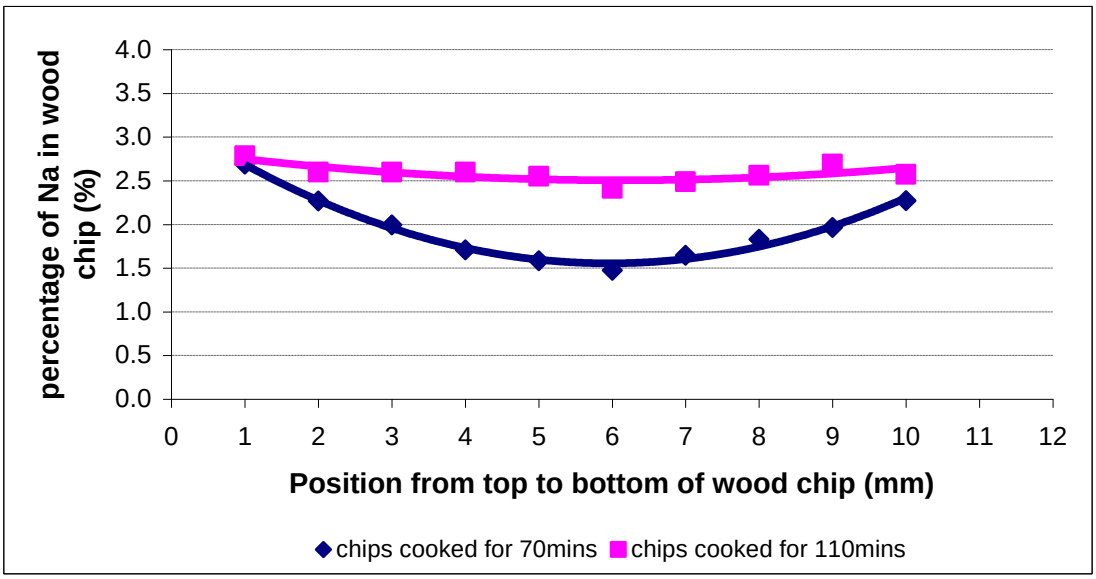

Figure 8. Average sodium content for three chips cooked for 70 and 110 minutes measured using ESEM/EDX.

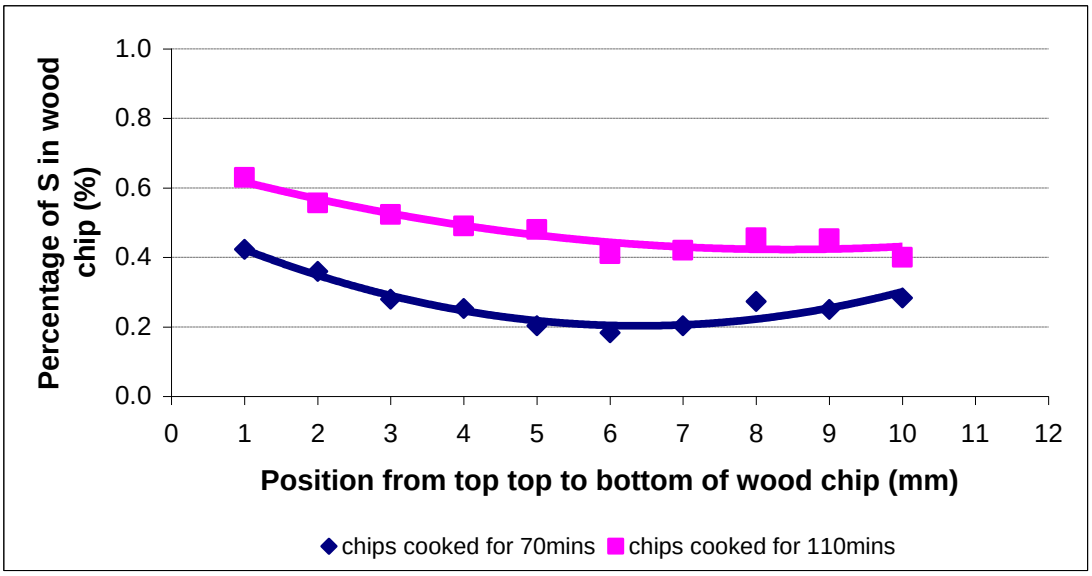

Figure 9. Average sulphur content for three chips cooked for 70 and 110 minutes measured using ESEM/EDX.

3.1.4 Repeatability of ESEM/EDX measurements

In order to test the repeatability of the ESEM/EDX method, two chips, one from the 70mins cook and the other from the 110mins cook, were sampled and measured for sodium and sulphur using ESEM/EDX. Five replicate measurements were carried out at the same position on each chip. The average sodium and sulphur concentrations are shown in Figures 10 and 11, respectively. The standard error was less than 0.6 % for sodium and less than 0.1% for sulphur measurement, indicating good repeatability of the method for both elements.

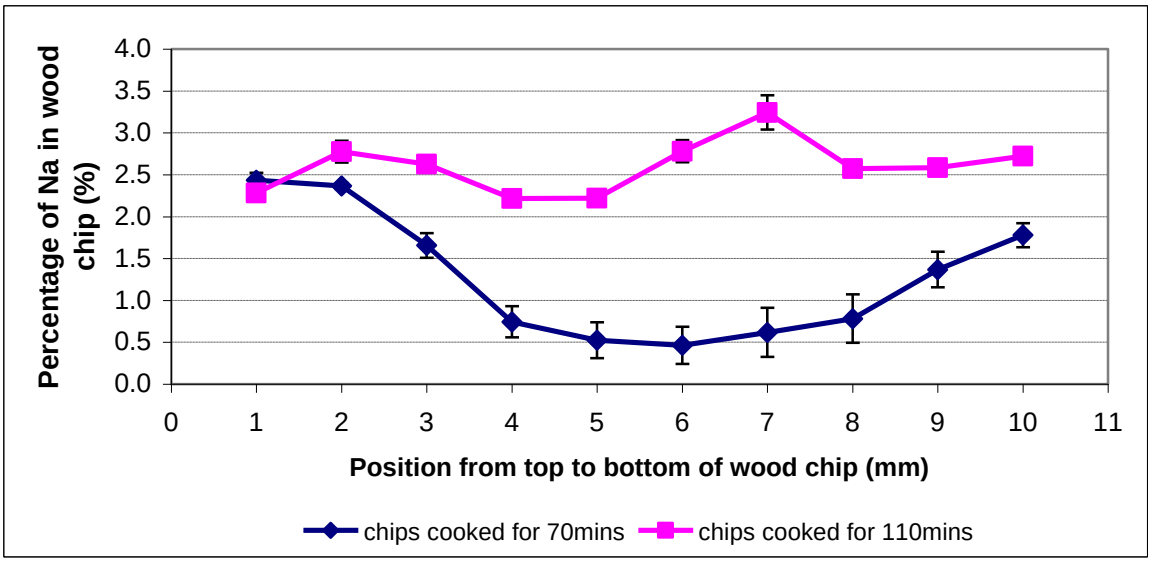

Figure 10. Sodium profile measured at different positions on the chip using ESEM/EDX. Error bars represent the standard error (n=5).

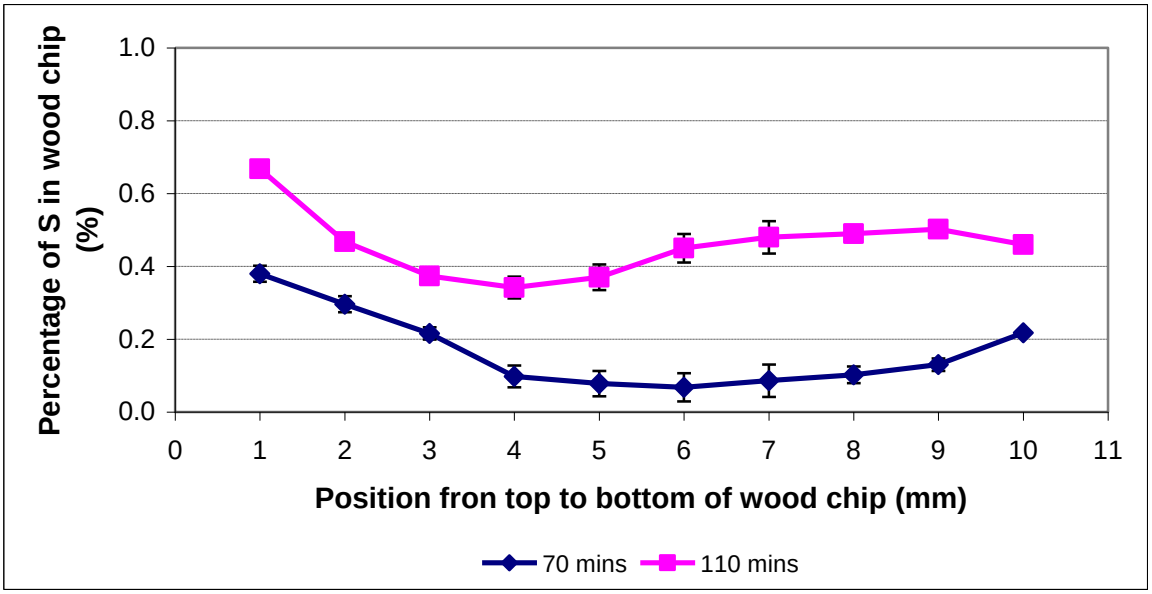

Figure 11. Sulphur profile measured at different positions on the chip using ESEM/EDX. Error bars represent the standard error (n=5).

3.2 Influence of pulping aids on liquor penetration and diffusion during kraft pulping

Figures 12 and 13 show the sodium and sulphur profiles in wood cubes cooked using the kraft process with and without pulping aids. Across all treatments, liquor penetration and diffusion was the greatest at the edge of the cubes with little or no penetration at the centre. The results show that there was some enhancement in penetration and diffusion into the cubes for

cooks treated with AQ, surfactant and a combination of both additives, compared to the control cook. However, the effect of surfactant on sulphur penetration and diffusion was less clear. In literature, there are some contradictory results on the benefits of surfactants. Some studies [15] reported little or no effect of surfactants on liquor pentration and diffusion efficiency, whilst others have reported improved pulping performance with the addition of such surface active agents to the cooking liquor [16-17].

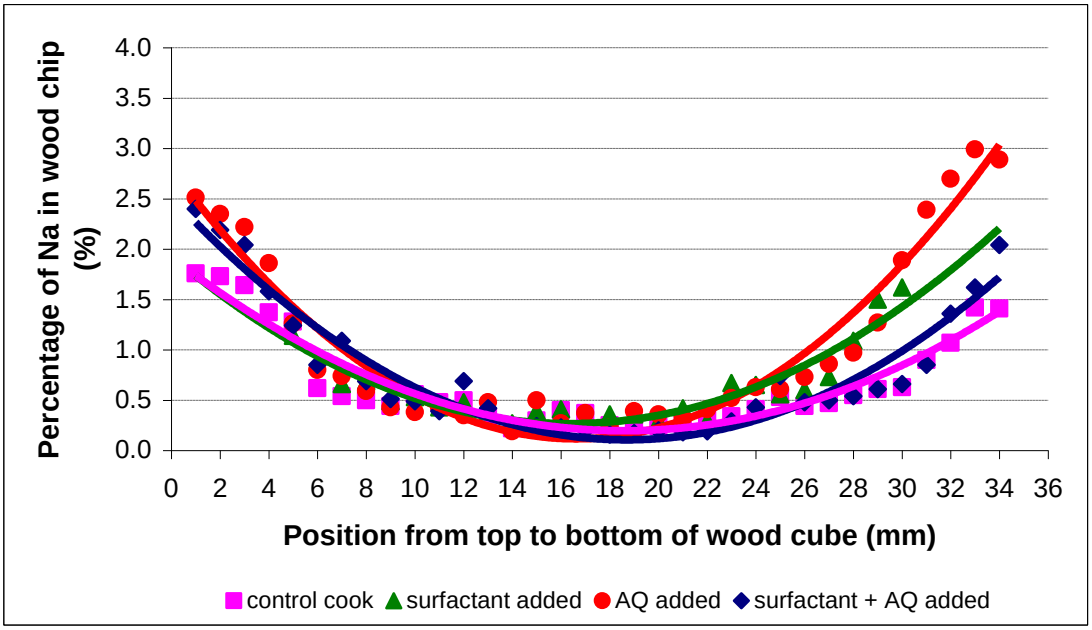

Figure 12. Sodium profile in cube after kraft pulping with and without pulping aids, as measured with ESEM/EDX.

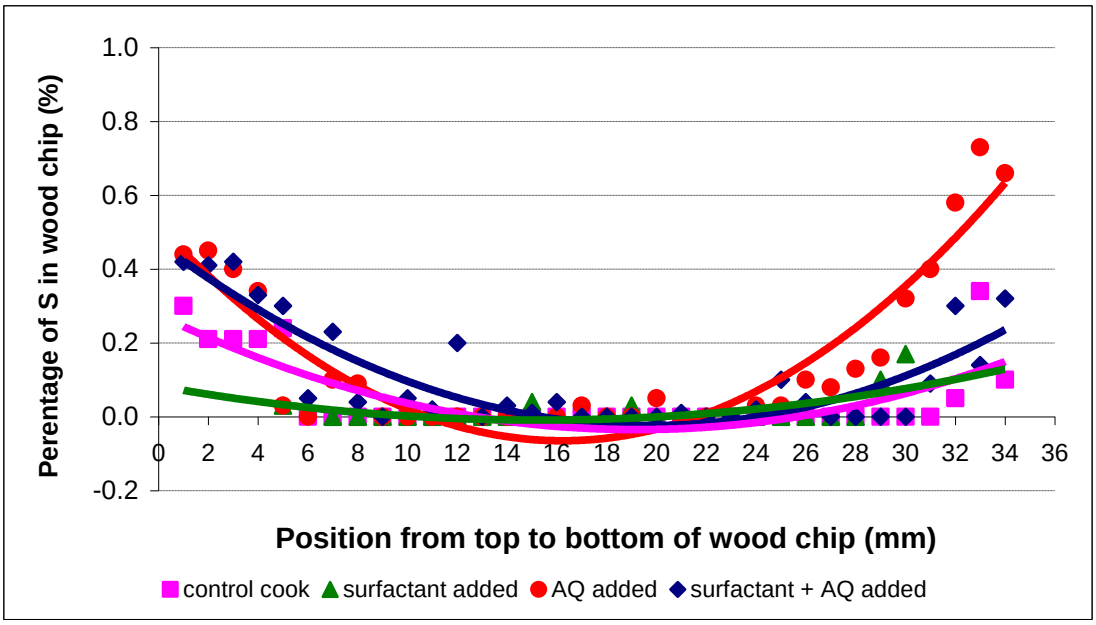

Figure 1. Sulphur profile in cube after kraft pulping with and without pulping aids, as measured with ESEM/EDX.

3.3 Influence of chip thickness on liquor penetration and diffusion during kraft pulping

The results in Figures 14 and 15 show that the sodium and sulphur contents were higher in the 4mm thick chips than in the 6mm thick chips. This was consistent with findings of other researchers [18] which showed that thicker wood chips impede liquor penetration and diffusion. In addition, the distribution of cooking liquor in the 4mm thick chips was more uniform, whereas in the case of the 6mm thick chips, the centre of the chips showed reduced levels of both elements. Non-uniform distribution of cooking liquor in thick chips often lead to non-uniform delignification, increased rejects, and decreased pulp yield and quality.

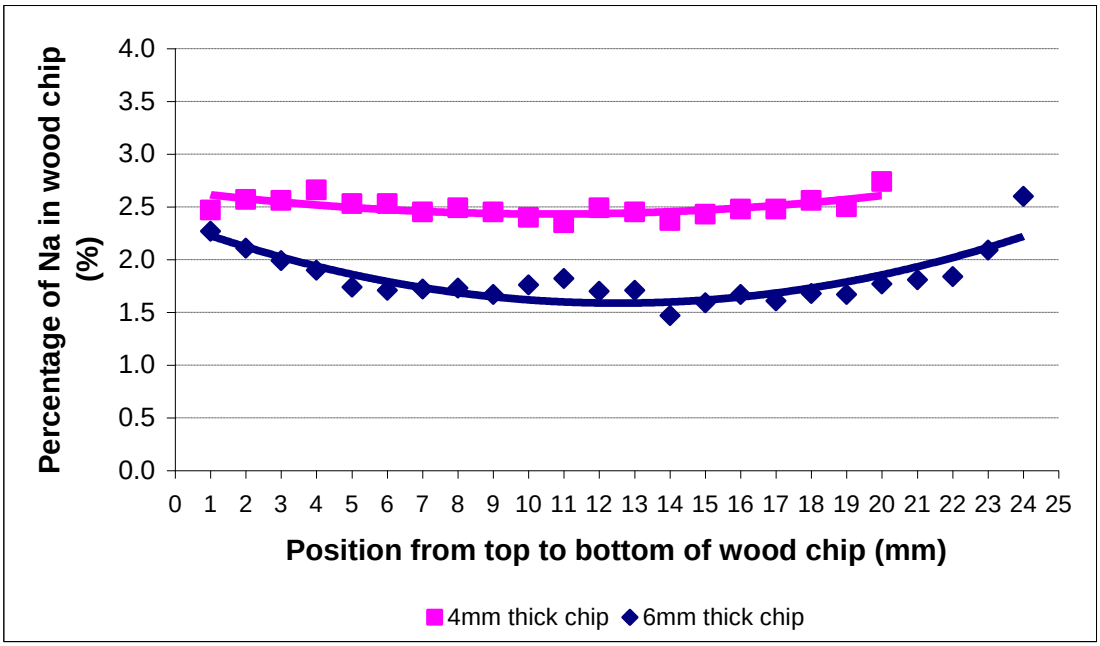

Figure 14.Sodium profile in 4mm thick chips compared to 6mm chips, as measured by ESEM/EDX.

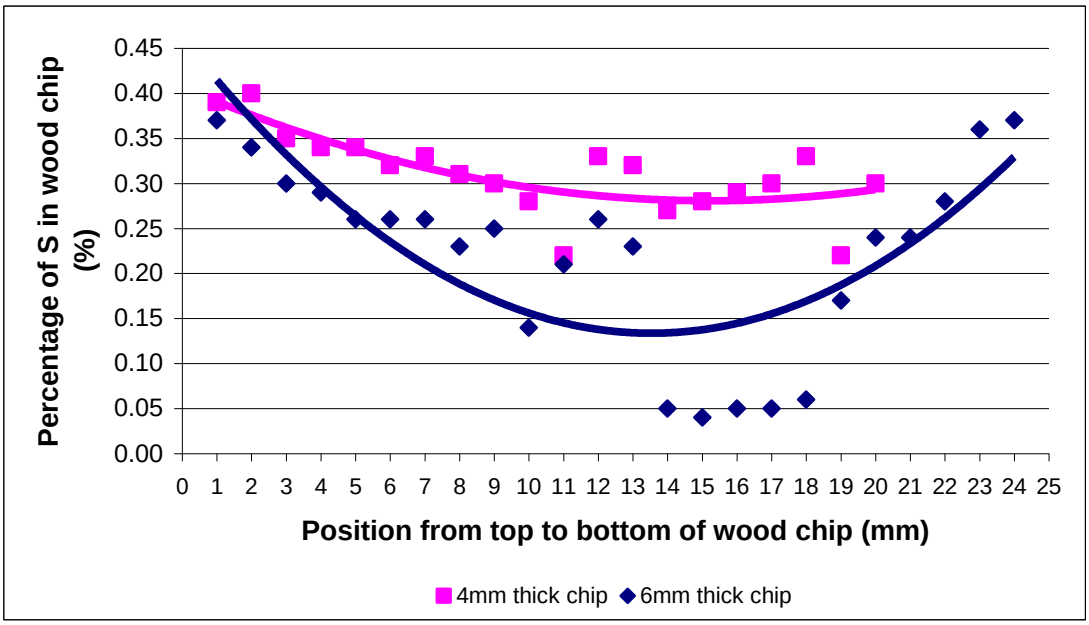

Figure 15. Sulphur profile in 4mm thick chips compared to 6mm thick chips, as measured by ESEM/EDX.

4. CONCLUSION

ESEM/EDX was optimised to measure the penetration and diffusion of cooking liquor into *Eucalyptus grandis* wood chips during kraft pulping. The moisture content of the cooked wood chips was found to influence the

measurement of sodium and sulphur. A possible explanation for this could be due to the concentration of oxygen being higher in the never dried chips due to its contribution from water. However, this needs further investigation. The contribution of sodium and sulphur already present in the wood prior to pulping was found to be negligible. Using the optimised ESEM/EDX method, investigations into the use of pulping aids during kraft pulping showed that the penetration and diffusion of sodium and sulphur was enhanced by the use of AQ and a combination of AQ and surfactant. However, according to the results, surfactant used on its own had little effect on sulphur penetration and diffusion. As expected, chip thickness influenced the penetration and diffusion of cooking liquor into the wood structure during cooking. ESEM/EDX measurements revealed improved and more uniform penetration and diffusion of cooking liquor for 4mm thick chips compared to 6mm thick chips.

5. ACKNOWLEDGEMENTS

Mondi and Sappi for their financial contribution to the project.
Buckman Laboratories for providing samples of AQ and surfactant.
University of KwaZulu Natal for ESEM/EDX analysis.

6. REFERENCES

1. Gierer J., (1980). Chemical aspects of kraft pulping. *Wood Sci. and Technol. 14: 241-266.*
2. Zanuttini M., Citroni M., Marzocchi V. and Inalbon C. (2005). Alkali impregnation of hardwood chips. *TAPPI J 4(2): 28–30.*
3. Jacobson A.J., Smith G.D., Young R. and Bannerjee S. (2006). Diffusion of sulfide into southern pine and sweetgum particles and chips. *Holzforchung 60(5): 498–502*.
4. Jimenez G., Chian D.S., McKean W.T. and Gustafson R.R. (1990). Experimental and theoretical studies to improve pulp uniformity. *Proceedings of the 1990 TAPPI Pulping Conference, Toronto, pg. 49 - 53.*
5. Greer C., Duggilara P. and Duffy B. (2004). Digester additives maximize pulping efficiency, reduce bleaching demand. *Online Pulp and Paper Mag, Sept 2004.* (*http://www.risiinfo.com/magazines/September/2004/PP/Digester-Additives-Maximize-Pulping-Efficiency-Reduce-Bleaching-*

Demand.html. *Date accessed 28 March 2011.*

6. Quinde A. (1994). Pulping additives in kraft pulping: Past, present and future. *Spring Conference Canadian Pulp and Paper Ass. Jasper, Alberta. May 19 – 21.*
7. Stamm A.J. (1953). Diffusion and penetration mechanism of liquids into wood. *Pulp and Paper Magazine of Canada 54(2): 54-63.*
8. Stone J.E. (1956). The penetrability of wood. *Pulp and Paper Magazine of Canada 57(7): 139-145.*
9. Sharareh S., Tessier P. and Lee C-L. (1996). Penetration of sodium sulphite into black spruce and aspen wood chips using SEM/EDXA. *J. Pulp and Paper Sci. 22(3): 71-77*.
10. Jensen W., Folgelberg B.C. and Johanson M. (1960). Studies on the possibilities of using radioactive tracers to follow the penetration of cooking liquors into wood. *Paperi ja Puu 42(7): 393-400.*
11. Zannuttini M., Citroni M., Marzocchi V. (2000). Pattern of alkali impregnation of poplar wood at moderate condition. *Holzforschung 54(6): 631–636*.
12. Dawson-Andoh B.E., Halloin J.M., Cooper T.G., Kamdem D.P., and Potchen E.J. (2001). Magnetic resonance imaging as a potential tool in the study of wood penetration by waterborne preservative systems. *Wood and Fiber Sci. 33(1): 84-89*.
13. Rudman P. (1965). Studies in wood preservation, Part I: The penetration of liquids into Eucalypt sapwoods. *Holzforschung 19(1): 5-13*.
14. http://www.itg.uiuc.edu/ms/equipment/microscopes/esem/how_it_works.htm. (Date accessed: 28 March 2011).
15. Kleinert, T.N. and Marraccini, L.M. 1965. Distribution of chemicals in commercial wood chips: alkaline pulping studies. *Tappi J. 48(3): 165-169*.
16. Parthasarathy, V.R., Grygotis, R.C., Wahoske, K.W., Bryer, D.M. 1996. A sulfur-free, chlorine-free alternative to kraft pulping. *Tappi J. 79(6):189-198.*
17. Duggirala, P.Y. 1999. Evaluation of surfactants as digester additives for kraft softwood pulping. *Tappi J. 82(11): 121-127.*
18. Dang, V.Q. and Nguyen, K.L. (2008). A universal kinetic model for characterisation of the effect of chip thickness on kraft pulping. *Bioresource Technol. 99:1486-1490.*