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EFFECTS OF PULP DRYING AND REFINING ON SOFTWOOD FIBRE WALL STRUCTURAL ORGANISATIONS

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ABSTRACT

Structural organisations of a range of softwood kraft and other pulps are described in terms of their response to pulp drying and refining. Fibre widths, thicknesses, wall thicknesses, and wall areas, as well as cross-sectional shapes can be very different depending on whether pulps are dried and/or refined. Fibres can also respond to refining in different ways depending on whether the fibres have thin or thick walls.

Actual cross-sectional wall areas (including void space associated with delaminations) of undried kraft fibres normally remain unchanged with refining whereas those of dried and rewetted For refined fibres, delaminated walls are fibres increase. envisaged as consisting of several concentrically oriented lamellae aggregates or coarse lamellae (containing wall substance plus water) interdispersed with void space filled predominantly with water. Thus, effects of pulp refining could be to make the structural organisation of the coarse lamellae but not the walls of undried kraft fibres more dense, and the walls of dried and Furthermore, the thicknesses of rewetted fibres less dense. uncollapsed, undried fibres normally decrease with pulp refining while those of collapsed, dried and rewetted fibres increase. Finally, cross-sectional shapes and dimensions of dried and rewetted, thick- and thin-walled fibres are modified in different ways and at different rates.

Wall organisations of kraft, soda-AQ and neutral sulphite-AQ (NSAQ) fibres are very different. Kraft fibre diameters (widths and thicknesses), wall thicknesses, wall areas and hemicellulose contents are substantially lower than those of NSAQ and soda-AQ fibres when compared at either the same lignin content or pulp yield. Effects of refining are to cause kraft fibre diameters to be decreased further, and walls to delaminate and expand into fibre lumens. The unique properties of kraft fibres are explained by a tightening and contraction of the fibrillar and lamella wall organisations.

Observed changes in fibre dimensions and behaviours are discussed in terms of fibre wall structural organisations, compositions and behaviours.

INTRODUCTION

Measurement of the fibre dimensions of width, thickness, wall thickness and wall area are useful in identifying and/or monitoring fibre qualities, and pulp drying and refining effects, as well as the collapse and flexibility potentials of different fibre-types (1,2,3). Recent studies have shown that effects of refining undried kraft fibres are tocause cross-sectional shapes to change from being generally angular to circular or oval, for overall diameters to decrease, and for the cross-sectional areas of fibre walls (which are apparently 'swollen' by refining) to normally remain unchanged. For dried and rewetted fibres, wall thicknesses, wall areas, and fibre thicknesses increase with refining, and collapsed fibre configurations partly revert to those of uncollapsed and undried refined fibres (1). In the present paper these, and additional data are interpreted with reference to current understandings of fibre properties and structures, and pulp drying and refining effects (6).

EXPERIMENTAL

Pulp preparation

All pulps were of commercial grade and consisted of radiata pine and other softwood fibre, except for the soda-anthraquinone (Soda-AQ), neutral sulphite-anthraquinone (NSAQ), and kraft sequence. The pulps of this sequence were rich in southern pine fibre and were prepared under the following laboratory conditions.

Kraft	Alkali charge:	18% (Na,O) active alkali (on wood)
	Sulphidity:	30%
	Liquor:wood:	4:1
	Max. temp:	170 C
	Time to temp:	90 min.
	H factors (appr	ox):800, 1000,1200, 1400, 1650
Soda-AQ	Alkali charge:	18% (Na,O) on wood
	AQ:	0.25% on wood
	Liquor:wood:	4:1
	Max. temp:	170 C
	Time to temp:	90 min.
	Time at temp:	30, 50, 70, 90, and 120 (approx.) mins.

The digesters were evacuated and flushed twice with nitrogen gas prior to heat-up.

NSAQ

Two different chemical charges were used in order to produce pulps over the kappa number range that was required. These were (i) 22% Na_2SQ_3 and 4.5% Na_2CQ_3 and (ii) 30% Na_2SQ_3 and 6.1% Na_2CQ_3 . For each series the liquor to wood ratio was 4:1 and the AQ charge was 0.25% on wood. The digesters were evacuated and flushed twice with nitrogen gas prior to heat-up. The pulping temperature was 175 C, heat-up time 90 minutes and time at temperature for series (i) was 20, 40, 90, and 150 minutes and for (ii) 120 and 180 minutes.

Pulp processing

Procedures for fibre processing, embedding, sectioning, and staining, and of the manual and image processing method for measuring fibre cross-section dimensions, have been described in detail elsewhere (1,2) and are not repeated herein. It is important to note that the data of Tables 4 and 6 were obtained using a manual procedure (2), whereas those of Tables 1, 2, 3, and 5 were obtained using an automated image processing method (1). Trends but not datum magnitudes obtained using the two measurements are comparable (1).

Pulps were normally dehydrated through an acetone series prior to embedding (1). To test whether fibre dimension differences for unrefined and refined pulps could be related to artifacts created during acetone dehydration, selected samples were also dehydrated using isopropanol (Lindstrom, pers. comm.) and isopropanol followed by n-pentane (4).

RESULTS

Undried kraft fibres

Refining effects on the cross-section dimensions of undried fibres in low yield kraft pulps are presented in Tables 1, 2 (Figure 1). Each pulp was prepared from radiata pine chips of different origin. Pulp refining causes fibre widths and thicknesses, and cross-sectional wall areas to decrease or remain unchanged. Wall thicknesses can decrease, increase or remain unchanged but usually increase (Tables 1, 2). Proportions of lumen also decrease with pulp refining (as expected) as fibre diameters decrease and walls delaminate and expand inwards (Tables 1, 2 Figure 2).



Fig. 1: Generalised fibre cross-sectional shapes of undried and uncollapsed fibres (a) and dried and rewetted, and collapsed fibres (b). The dimensions of thickness and width are indicated.

Dehydration of either unrefined or refined pulps in acetone, isopropanol or isopropanal followed by n-pentane has no effect on fibre widths or thicknesses (Table 2). Wall areas, wall thicknesses, and proportions of lumen are, however, strongly affected by the dehydration medium. Trends for, and differences between, the cross-sectional dimensions of unrefined and refined fibres are generally independent of pulp dehydration procedure.

Qualitative examination of paired photomicrographs also shows that pulp refining causes fibre cross-sectional shapes to become circular or oval, for diameters to decrease, and walls to be delaminated (Figure 2).



Fig. 2: Cross-sectional shapes of unrefined and refined, undried fibres. Extensive delamination of fibre walls is seen for the refined fibres. Refined pulp processed for 8000 rev. in PFI mill at 10% stock concentration and a load of 1.8 N/mm.

		(mu)	TULCKNE	(mu) ss	INTIN TTPM	tuess (μm)	Wall ar	еа (µm2)		
5	Inrefined	Refined	Unrefined	Refined	Unrefined	Refined	Unrefined	Refined	Unrefined	Refined
m	31.2	30.3	18.9	18.2	4.4	4.9	337	346	22.7	17.1
ന	30.1	28.8	19.5	16.3	4.6	4.3	329	283	26.0	16.6
~	29.1	27.4	18.6	17.0	4.3	4.4	298	284	26.7	17.9
en	32.1	29.0	16.2	14.1	3.7	3.5	265	225	24.1	19.8
SD	1.7		1.1		0.3		26.6	10	2.	1

TABLE 1: Refining effects on the fibre cross-sectional dimensions of undried kraft fibres*

Unrefined Refined Wrrefined Norefined Ref cetone I 29.2 30.3 15.3 14. II 29.4 29.8 15.9 14. III 20.7 30.4 16.2 15. iII 30.7 30.4 16.2 15. sopropanol I 31.3 31.6 16.5 15. isopropanol I 31.3 31.6 16.5 15. III 31.3 31.2 16.5 15. 15. isopropanol I 31.2 17.6 16. 16.5 15.	Unrefined Refined 15.3 14.4 15.9 14.2 16.2 15.2 16.5 15.1	Unrefined 3.3.3 3.6 3.9	Refined: 3.7 4.2 4.2 4.1	Unrefined 226 244 273 273	Refined 250 268 283 283 288	26.7 24.0 22.0	19.4 14.4 15.9
cetone I 29.2 30.3 15.3 14. II 29.4 29.8 15.9 14. III 30.7 30.4 16.2 15. III 30.7 30.4 16.2 15. sopropanol I 31.3 31.6 16.5 15. iii 33.2 31.6 16.5 15. 15. iii 33.2 31.2 16.5 15. 15. iii 31.8 31.2 17.6 16. 16.	15.3 14.4 15.9 14.2 16.2 15.2 16.5 15.1	ო. ს. თ. თ. ო. ო. ო. ო. ო. ო.	3.7 4.2 4.1	226 244 273 269	2550 28833 288	26.7 24.0 22.0	19.4 14.4 15.9
II 29.4 29.8 15.9 14. III 30.7 30.4 16.2 15. sopropanol I 31.3 31.6 16.5 15. II 33.2 31.2 16.5 15. II 31.8 31.2 16.5 16.	15.9 14.2 16.2 15.2 16.5 15.1	6. 6. 6. 6. 6. 6.	4.2 4.2 4.1	244 273 269	268 283 288	24.0 22.0	14.4 15.9
III 30.7 30.4 16.2 15. sopropanol I 31.3 31.6 16.5 15. II 33.2 31.2 16.5 15. III 31.8 31.2 17.6 16.	16.2 15.2 16.5 15.1	6. 6. 6. 6. 6.	4.2	273 269	283 288 288	22.0	15.9
sopropanol I 31.3 31.6 16.5 15. II 33.2 31.2 16.5 15. III 31.8 31.2 17.6 16.	16.5 15.1	3.9	4.1	269	288	50	
sopropanol I 31.3 31.6 16.5 15. II 33.2 31.2 16.5 15. III 31.8 31.2 17.6 16.	16.5 15.1	3.9	4.1	269	288	26 7	
II 33.2 31.2 16.5 13. III 31.8 31.2 17.6 16.						1.02	17.6
III 31.8 31.2 17.6 16.	16.5 15.6	4.1	4.5	295	309	24.0	13.2
	17.6 16.5	4.5	4.6	318	310	22.5	17.0
sopropanol I 30.0 30.8 15.4 14.	15.4 14.2	3.7	3.8	246	254	24.4	17.1
lus n-pentaneII 31.9 30.6 16.1 14.	16.1 14.7	3.9	4.2	275	277	21.1	13.7
III 31.4 30.5 17.0 16.	17.0 16.1	4.3	4.6	303	305	20.4	15.1
1.0 1.0	1.0	0.3		25		2.0	

TABLE 2: Dehydration solvent effects of cross-section dimensions of undried kraft fibres*

Measurements made using image processing (1). Least significant difference between means at the 95% level. Refined in Fit mill for 8000 rev. with an applied load of 1.8 N/mm.

* + .

Pulp		Pulp co	mpositic	(%) uc			Fibre c	es-sei	ction din	tensions			Proportion	lumen (%)
rype Yie	ld Klason	Percent	total (carbohydrates	Width	(มา1่)	Thicknes	(штf) s.	Wall thic	ckness (µm)	LLaW (area (μm³)	Unref.	Ref.‡
	итибтт	Glucan	Xylan	Mannan	Unref.	t.1ef	Unref.	Ref.‡	Unref.	Ref.‡	Б	nref.Ref.‡		
Kraft 60.	4 18.0	85.8	8.2	6.0	32.3	33.2	21.4	19.5	4.8	4.9	398	386	24.1	19.1
57.	9 15.8	87.2	7.6	5.2	32.5	32.2	21.9	18.8	4.7	5.1	399	386	25.3	16.8
53.	1 12.4	83.4	9.3	7.3	32.1	33.4	20.9	19.1	4.6	5.0	369	379	26.4	18.9
49.	0 5.3	86.8	7.3	5.9	31.3	30.3	19.0	18.2	4.5	4.8	339	344	22.7	17.2
Soda-AQ 60.	.0 15.3	81.7	8.7	9.6	34.2	34.8	23.0	20.3	5.6	5.7	457	443	23.2	17.7
55.	7.9 6.	83.0	7.8	9.2	33.4	32.5	22.1	19.3	5.3	5.3	430	401	23.0	15.4
53.	.2 9.1	83.3	7.0	9.7	32.8	33.7	22.2	19.1	5.3	5.5	427	400	24.3	15.9
49.	.1 6.2	84.4	6.9	8.7	33.0	31.3	20.2	18.9	5.1	5.0	392	365	21.4	17.0
48	.4 4.3	84.8	7.3	7.9	31.7	31.9	19.2	18.7	5.0	5.2	356	375	22.3	16.6
Neutral 61	.2 6.8	77.5	8.7	13.7	34.4	34.4	22.0	21.6	5.5	5.6	439	460	23.9	18.7
sulphite-AQ 58	.8 4.7	79.1	9.2	11.7	33.4	33.2	21.9	21.0	5.4	5.7	425	438	24.6	18.4
56	.4 5.9	7.67	8.0	12.3	33.9	33.6	20.4	20.9	5.1	5.5	402	438	24.1	18.4
54	.3 4.0	80.5	8.9	10.6	33.0	33.4	20.0	20.8	4.7	5.5	363	437	26.4	18.7
*ISD					1.9		1.1		0.3		34		2.	_

TABLE 3: Pulping process effects on fibre cross-section dimensions

Least significant difference between means at the 95% level. Refined in FFI mill for 8000 rev. with an applied load of 1.8 N/mm.

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Undried fibres-kraft, soda-AQ, and neutral sulphite-AQ

With decreasing pulp yields, fibre widths change slightly whereas fibre thicknesses generally decrease (Table 3). Fibre thicknesses and widths are least for the kraft furnishes, particularly for the furnishes of higher yield. Fibre wall areas and wall thicknesses also decrease with decreasing pulp yields. Actual fibre width and wall areas for the neutral sulphite-AQ (NSAQ) and soda-AQ furnishes are significantly greater than for those of the kraft pulps. Also, when compared at equivalent lignin contents, soda-AQ and NSAQ fibre widths, wall areas, and wall thicknesses are similar.

Wall areas are generally unchanged or decreased by refining except for the NSAQ furnishes where wall areas are increased, particularly at low yields. Wall thicknesses normally increase slightly with refining as fibre thicknesses decrease and walls swell inwards into fibre lumens. Proportions of lumen indicate the extent to which wall mass expands into fibre lumens with refining. As kraft and soda-AQ fibre thicknesses and overall diameters decrease with refining, proportions of lumen can also decrease markedly, even though overall wall areas are normally unchanged. Alternatively, with refining, NSAQ lumen proportions are decreased, wall areas increased, and fibre thicknesses unchanged.

For all pulps xylan contents are similar although the kraft and soda-AQ values could be slightly lower than those of the NSAQ pulps. Mannan contents are greatest for the NSAQ followed by the soda-AQ and the kraft furnishes.

Clear differences between pulps of similar lignin content are shown in the micrographs of Figure 3. The thick walls of the NSAQ and soda-AQ pulps are evident as are the swollen and delaminated wall configurations of the refined NSAQ fibres. The walls of the soda-AQ fibres are modified least by pulp refining.

Drying effects

The fibre cross-section dimensions of two pairs of undried, and dried and rewetted kraft pulps are presented in Table 4. Based on fibre thickness values (Table 4) and visual appearance (Figure 4), the dried and rewetted fibres are clearly more collapsed than those in the corresponding undried pulps. Fibre wall thicknesses are significantly reduced by pulp drying whereas fibre widths are unchanged.



Fig. 3: Cross-sectional shapes of undried kraft, soda-AQ and NSAQ fibres.



Fig. 4: Cross-sectional shapes of undried, and dried and rewetted fibres.

Pulp treatment	Fibre thickness	Fibre width	Fibre wall thickness
	(m)	(Mm)	(Mm)
Undried	21.6	44.4	4.0
Dried & rewetted	11.4	44.3	3.1
Undried	24.4	45.3	4.7
Dried & rewetted	15.9	44.1	4.3
† LSD	1.5	2.6	0.5

* Measurements made manually (2).

† Least significant difference between means at 95% level.

TBALE 4: Cross-section dimensions of undried, and dried and rewetted radiata pine kraft fibres*

Dried and rewetted fibres

Effects of refining on the fibre cross-section dimensions of a range of dried and rewetted softwood kraft pulps (Table 5) are very different from those of undried pulps (Tables 1, 2). For the dried and rewetted fibres, widths are normally unchanged while thicknesses, wall thicknesses and wall areas increase with pulp refining (Table 5). Market kraft pulps which represent a wide range of softwood fibre types and cross-section dimensions are classified as pulps 1 to 8 (Table 5) and pulps A, B, and C (Table 6).

Cross-section shapes and dimensions of dried and rewetted thick- and thin-walled fibres are modified by pulp refining in different ways and at different rates (Figures 5 to 11) (Table 6). Thin-walled fibres partly retain their collapsed configurations with refining whereas those of thick-walled fibres become circular and uncollapsed (Figures 5, 6). For both thin- and thick-walled fibres, walls are swollen, and thicknesses and widths increase and decrease respectively, although in different ways and at different rates (Figures 7,8,9). Changes in fibre cross-section shapes and dimensions brought about by pulp refining are most rapid during early stages of treatment but vary with fibre wall thicknesses (Table 6, Figures 7,8,9).

Fibre and wall thickness population distribution curves for the unrefined and refined pulps of Table 6 are very different (Figures 10,11). Pulp 'A' contains high proportions of thin-walled and collapsed fibres while pulp 'B' contains relatively high proportions of both thin- and thick-walled, and collapsed and

Pulp	PFI mill refining†	Fibre width (µm)	Fibre thickness (µm)	Wall area (µm²)	Wall thickness (µm)	Proportion lumen (%)	
1	Unrefined	25.1	8.6	121	2.4	10.6	
	Refined	26.7	10.0	162	3.1	8.6	
2	Unrefined	28.0	11.0	185	3.1	10.7	
	Refined	27.4	12.5	214	3.5	12.8	
3	Unrefined	24.3	8.8	124	2.5	9.5	
	Refined	25.0	10.0	145	2.8	9.4	
4	Unrefined	28.4	10.9	187	3.3	9.0	
	Refined	27.7	12.8	213	3.6	14.4	
6	Unrefined	29.0	10.8	185	3.1	11.8	
	Refined	27.3	13.0	206	3.3	16.8	
7	Unrefined	27.2	9.2	145	2.6	9.3	
	Refined	26.2	10.4	162	3.0	10.9	
8	Unrefined	30.0	13.9	263	4.4	8.9	
	Refined	26.3	15.2	265	4.6	9.2	
‡LSD		1.8	0.8	18	0.25	1.5	

*

Measurements made using image processing (1). PFI mill at 10 percent consistency with an applied load of 3.3 N/mm for 8000 rev. Least significant difference between means at 95 percent level. t

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TABLE 5: Refining effects on the fibre cross-section dimensions of a range of bleached, dried and rewetted softwood kraft pulps*

uncollapsed fibres. Fibre thickness values give an indirect measure of fibre collapse. The broad distribution curves of the unrefined 'B' fibres become broader with refining and also show a tendency to be bimodal.

PFI mill		Pulp 'A'			Pulp'B'			Pulp 'C'	
refining	t Fibre width (μm)	Fibre thickness (μm)	Wall thickness (µm)	Fibre width (µm)	Fibre thickness (µm)	Wall thickness (μm)	Fibre width (μm)	Fibre thickness (µm)	Wall thickness (µm)
0	33.8	£.6	2.8	36.8	14.9	4.7	39.2	13.2	3.9
1000	33.0	10.3	2.9	37.9	15.3	4.8	39.4	14.7	4.1
2000	34.5	10.5	3.0	34.0	16.0	5.1	37.8	15.5	4.3
4000	32.4	10.9	3.1	34.0	16.4	5.1	38.3	15.6	4.2
8000	32.3	11.1	3.3	34.6	17.2	5.5	34.2	15.4	4.5
16000	32.8	11.3	3.1	32.8	17.8	5.4	35.6	15.8	4.6
* +-	Least significan Measurements madé PFI mill at 10 pé	t difference at 9 e manually (2). ercent consistenc	15 percent level sy and an applie	: fibre width 2. d load of 3.3 N/m	7 µm, fibre thic m.	ckness 1.1 µm, a	nd wall thickness	0.4 µm.	

TABLE 6: Refining effects on the fibre cross-section dimensions of bleached, dried and rewetted, softwood kraft pulps*



Fig. 5: Refining effects on the cross-section configurations of a dried and rewetted furnish which contains a high proportion of thin-walled fibres. Refined pulp processed for 8000 rev. in a PFI mill at 10% stock concentration and a load of 3.3 N/mm.



Fig. 6: Refining effects on the cross-section configurations of a dried and rewetted furnish which contains relatively high proportions of thick-walled fibres. Refining conditions as for Fig. 4.











DISCUSSION

Dehydration effects

For unrefined fibres, widths and thicknesses are generally independent of the different dehydration conditions used (Table 2). Thus, changes in fibre wall specific surface and pore structure brought about by different dehydration media, or by the presence of residual non-exchanged water in fibre walls, are not reflected the fibre diameter parameters of width and thickness. in Replacement of acetone with the less polar isopropanol (or isopropanol followed by n-pentane) shows that the acetone dehydration causes fibre wall areas and thicknesses to shrink. Relative to effects of isopropanol, pulp dehydration using acetone causes fibre walls to contract from the lumen side. Whether the isopropanol wall area and thickness, and lumen proportion data represent true and absolute values for water swollen fibres is uncertain (4, 5), although they can be considered comparable.

Wall area and thickness, and lumen proportions for refined and unrefined fibres are very different for pulps dehydrated in acetone and isopropanol (or isopropanol followed by n-pentane) (Table 2). Qualitative effects of refining are, however, similar and independent of the dehydration solvent used. Thus, measured effects of refining on undried fibre cross-section dimensions (fibres dehydrated in acetone) are considered to be qualitatively real and meaningful (Tables 1, 2).

Effects of refining undried kraft fibres

Effects of refining undried kraft fibres are to cause angular fibre cross-sectional shapes to become circular, and for fibre walls to delaminate and expand inwards into fibre lumens (8,9). Expansion of fibre walls outward is prevented by the retention of the S1 layer even after extensive refining (8). For the low yield kraft fibres, PFI mill refining removes less than 20% only of the S1 layer from fibre surfaces (7).

Observations and quantitative dimension data described herein confirm the earlier findings of McIntosh (8), and of Page and de Grace (9), and highlight some new effects of pulp refining:

1. Fibre widths and thicknesses are decreased by pulp refining.

 Fibre walls delaminate and expand into lumens, but mean wall areas are normally unchanged by pulp refining. Wall thicknesses can increase as diameters decrease and fibre walls expand into the available lumen space.

Fibre diameter: The measured decreases in fibre thickness and width (Tables 1,2) are conservative estimates of overall decreases in fibre diameter or fibre cross-section area (wall plus lumen area). The minimum rectangle measurements of fibre width and thickness (1) do not take into account the changes in cross-section shape which take place; from angular-rectangular to roundedcircular.

The decrease in fibre width and thickness brought about by pulp refining is considered to be related, in part, to a tightening of the outer S1 layer and/or the bulk of the fibre wall (the S2 layer). The S1 layer of fibre walls consists of several lamellae with microfibrils oriented at a range of angles to fibre axes (10,11). During pulp refining, structural organisations of fibre walls are modified. For the S1 layer at least, such modifications must result in a substantial tightening of outermost surface layers and shrinkage of fibre cross-section perimeters, probably through a lateral contraction of lamellae at right angles to fibrillar orientations (Figure 2). At the same time the bulk of the fibre wall, the S2 layer, must also be modified. Fibril angles decrease relative to fibre axes as a result of pulp refining (12); an effect which may cause S2 layer thicknesses to contract. Furthermore, if differential changes in fibrillar angles occur, or stress concentrations develop, within the walls of individual fibres during pulp refining, intralayer separation or delamination would result.

Wall delamination and shrinkage: During pulp refining, structural modification and reorganisation of the outer layers of fibre walls takes place and fibre cross-section perimeters and fibre widths and/or thicknesses decrease. At the same time the structural organisation of the bulk of the fibre wall, the S2 layer, is also modified and can delaminate into one or several concentric layers. As a result of the removal of wall material during pulping, the walls of undried, low yield kraft fibres are porous and consist of more water than wall substance in a ratio of about 55:45 (13,14). Pulp refining causes further increases in the relative proportions of water in fibre walls (15), and therefore, fibre wall crosssectional areas could also be expected to increase. This is not the case (Tables 1,2) and an explanation is as follows: The increase in kraft fibre wall volumes which occurs with pulp refining is relatively small (15), and could be masked by possible artifacts created during sample dehydration and preparation, and/ or by the insensitivity of the measurement procedure. It is, however, noteworthy that kraft and sulphite fibre wall volume differences, as measured by Stone and Scallan using techniques of solute exclusion (14), are roughly equivalent to those of the unrefined kraft and NSAQ fibres listed in Table 3. Furthermore, effects of pulp refining are to increase the wall volumes of sulphite fibres more than those of kraft (15), an effect also shown for the kraft and NSAQ wall area data (Table 3). The absence of a measurable change in wall area through refining the kraft fibres (Table 3) is, therefore, somewhat surprising.

Irrespective of whether or not kraft fibre wall areas are unchanged (Tables 1, 2, and 3) or increased slightly by pulp refining the following comments must apply. During refining the S2 layers of fibre walls delaminate and expand into fibre lumens (Table 1). As these effects of refining occur, overall proportions of water in total wall volumes are increased and redistributed as void spaces associated with wall delamination are filled (8,9) (Figure 2). It is proposed that stresses develop within fibre walls as a result of pulp refining and relatively coarse delamination Within the coarse lamellae, so developed, it is takes place. reasoned that reorganisation of structural elements (cellulose microfibrils and microfibril aggregates) takes place, void-space or microvoid volumes decrease, specific surfaces increase, and coarse lamellae densities actually increase with refining. Based on the cell wall models of Kerr and Goring (17) and Scallan (16,18) such a possibility cannot be discounted. Thus, the coarse lamellae could consist of multilayered bands of tangentially, and to a lesser extent radially, oriented bands of cellulose microfibrils and associated lignin and hemicellulose residues. During pulp refining two levels of structural reorganisation, therefore, take (i) place: Fibre walls can delaminate into one or more concentrically arranged bands of coarse lamellae which can be considered as being essentially separate one-from-another, and (ii) within each coarse lamellae, densification takes place with structural reorganisation and the collapse or partial collapse and redistribution of wall microvoids.

The hypothesis that pulp refining causes a densification of the coarse lamellae through structural reorganisation cannot be discounted because of the parallel development of increased fibre

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flexibility and increased fibre wall specific surface and waterholding ability. During refining, coarse lamellae move and flex relative to one another, inter- and intra-lamellae fibrillation takes place, and fibre wall water-holding and wetting abilities increase (6, 15). Similarly, structural elements within the coarse lamellae are able to move relative to one another during pulp refining, and packing arrangements are greatly changed from those in pulped but unrefined fibres. Thus, void sizes and numbers probably decrease and increase respectively and the water in unrefined fibre walls is redistributed during refining and becomes more intimately associated with the various constituents of the coarse wall lamellae (cellulose, hemicellulose, and lignin). With pulp refining, therefore, fibres are envisaged as becoming more flexible as walls delaminate and structural wall elements, wall components, and water within the coarse lamellae are redistributed and interact one-to-another in different ways and at different levels (microstructural, ultrastructural, and molecular). It is, therefore, reasoned that such an array of interactive effects of refining could cause fibres to be plasticised and made flexible, for fibre wall specific surfaces and water-holding capacities to be increased, but for fibre wall volumes and cross-sectional areas to be changed only slightly. Such conclusions are either supported or not contradicted by the following findings of Stone et al(15): (i) there is an appreciable volume of water (0.4 g/g) in pores smaller than 0.0025 m and that this volume is unchanged by pulp refining, (ii) pulp refining causes an increase in the volume of water in pores in the range 0.0025 to 0.0560 m, and (iii) based on techniques of solute exclusion, the walls of undried kraft fibres swelled slightly in the initial period of refining and thereafter stayed constant throughout the refining treatment.

Effects of refining undried kraft, NSAQ, and soda-AQ fibres

When compared at equivalent lignin contents or pulp yields, fibre widths, thicknesses, wall areas, and wall thicknesses are lower for the kraft than for the soda-AQ or NSAQ pulps (Table 3). Hemicellulose contents are greatest for the NSAQ and least for the kraft pulps. The fibre cross-section dimension differences for the three pulp-types show that the kraft process somehow causes fibre diameters and wall areas and thicknesses to contract relative to soda-AQ and NSAQ pulping. Such differences in fibre wall structural organisations are reflected in their response to pulp refining with NSAQ fibre diameters being unchanged and those of kraft fibres decreasing as cross-sectional shapes become more circular and fibre walls delaminate and expand inwards into fibre lumens (Figure 2). Furthermore, NSAQ wall areas increase with refining whereas those of corresponding kraft fibres normally remain unchanged (Table 3). Wall thicknesses, on the other hand, increase for both types with refining. Magnitudes of wall delamination appear to be greater for the NSAQ than for the kraft fibres (Figure 3). In contrast, soda-AQ fibres show a low incidence of wall delamination, and wall thicknesses and wall areas remain unchanged with pulp refining when compared with the NSAQ and kraft fibres.

It is noteworthy that for lignin contents of 5 to 6% and pulp yields of about 49%, hemicellulose contents are higher for the soda-AQ than the kraft pulps. The response to refining is, however, lower for the soda-AQ than the kraft when measured in terms of wall delamination and wall thickness increases (Figure 3, Table 3). For the NSAQ fibres, on the other hand, a high hemicellulose content appears to correlate with ease of wall delamination and an increase in cross-sectional wall area.

Structural organisations and compositions of fibre walls are very different for the three pulp types (Table 3, Figure 3). Based on the data presented herein it would appear that the unique properties of kraft fibres (high paper tearing resistance and tensile strength) could be related to a tightening of the fibrillar spiral of the S2 layer during pulping, through longitudinal shrinkage of the composite fibrillar structure and/or lateral contraction of the lamellae elements which constitute fibre walls (16,17,18). Similar mechanisms will explain the situation where fibrillar angles are high and aligned roughly in the direction of fibre axes. Such contractions of fibre wall fibrillar and structural organisations will cause overall fibre and lumen diameters to decrease. In response to pulp refining, further tightening and contraction of the fibrillar and lamella structure is envisaged as differential stresses develop within fibre walls, concentric delamination occurs, walls expand inwards into lumens, and overall fibre diameters decrease further. Such behaviours of kraft fibres must be correlated with the selective removal of wall material during pulping, and lignin, hemicellulose and cellulose contents, distributions and chemical compositions.

Fibre cross section dimensions for the kraft, NSAQ and soda-AQ pulps (refined and unrefined) (Table 3, Figure 3) show trends and behaviours roughly similar to those obtained by Stone and

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Scallan (using techniques of solute exclusion) for kraft and sulphite pulps (13,14,15). Furthermore, explanations given by Stone and Scallan concerning fibre wall structural organisations and the roles of the lignin, hemicellulose, and cellulose wall components during both pulping (14) and refining (15), are also generally applicable to the cross section data of Table 3. Finally, fibre thicknesses but not widths decrease with decreasing NSAQ, soda-AQ, and kraft pulp yields; effects not observed for kraft and sulphite pulps by Stone and Scallan (13).

Effects of pulp drying

Effects of drying unbleached pulps are to cause fibre thicknesses and fibre wall thicknesses to decrease, and fibre widths to remain unchanged (2) (Table 4). Pulp samples were collected immediately before and after drying on a conventional pulp dryer. Web pressing, water removal, and drying processes cause fibres to be collapsed to significant extents (Figure 3). Extents of fibre collapse brought about by pulp drying are quantifiable through the measurement of changes in fibre thickness (Table 4). The walls of unbleached kraft fibres are highly porous (14,15) and are densified by pulp drying processes as structural elements within fibre walls are pulled together and bonded one to another, and pore volumes are greatly decreased and redistributed. Quantitative estimates of extents of wall densification brought about by pulp drying are measured as changes in fibre wall thickness (Table 4).

The similar undried, and dried and rewetted fibre widths are somewhat fortuitous. Undried fibre widths represent the maximum dimension of the cross-section rectangle (Figure 10). Dried and rewetted fibre widths, on the other hand, represent the maximum dimension of the collapsed wall and this normally has as its origin the diagonal of the undried cross-section rectangle. This decreases in magnitude during drying as walls contract and the fibre collapses.

Effects of refining dried and rewetted fibres

Cross-sectional shapes of dried and rewetted fibres are generally collapsed (Figures 1, 4, 10) and their walls densified (Table 4) compared with undried fibres. Furthermore, fibre and wall thicknesses increase and fibre widths normally change only slightly with pulp refining (Table 5). The response to refining



Fig. 10: Drying effects on fibre cross-section dimensions and shape.

of dried and rewetted fibres contrasts markedly with that of undried fibres where fibre thicknesses and wall areas generally contract rather than expand. For both the dried and rewetted, and the undried fibres, pulp refining causes walls to delaminate (Figures 2,5,6) although actual wall lamellae and/or lamellae aggregate densities decrease and increase respectively. Irrespective of their response to refining, actual extents of wall delamination and overall fibre flexibilities could be similar after refining for the two types of fibre. This has, however, not been measured.

For dried and rewetted fibres, observed effects of pulp refining are in agreement with conventional viewpoints (6): fibre wall structural organisations are modified as they are flexed and penetrated and rewetted with water, intra-wall bonds are broken, and walls become swollen, delaminated, plasticised, and flexible.

Mean fibre dimensions only are presented in Table 5 and effects of refining thick- and thin-walled fibres are not separable. Cross-sectional shapes of thin- and thick-walled fibres are, however, modified by refining to different extents and at different rates (Table 6, Figures 5 to 12).

Thin, and mixed thin- and thick-walled fibre populations respond differently to pulp refining as shown by the respective behaviours of pulp 'A' and 'B' (Figures 5,6,11,12,). Crosssectional configurations of thick-walled fibres become circular as their walls delaminate and expand outwards, fibre thicknesses



Fig. 11: Fibre thickness population distributions.

FIBRE WALL THICKNESS



Fig. 12: Fibre wall thickness population distributions.

increase or extents of collapse decrease. Thin-walled fibres, on the other hand, tend to retain their rectangular or collapsed cross-sectional shapes as walls and thicknesses expand outwards. Thus, thick-walled fibres revert to their uncollapsed configurations the most readily with refining.

For dried and rewetted fibres, thicknesses increase and walls swell and expand outwards most rapidly during early stages of pulp refining (Tables 5, 6, Figures 7,8). Different wall and fibre thicknesses and their response to refining can generally be related to different fibre wall masses. Fibre width behaviours, on the other hand, are very different for the three pulps of Table 6 (Figure 9). Pulp 'B' shows an abrupt decrease in width during early stages of refining. Pulp 'C' which contains wider but thinnerwalled fibres than Pulp 'B' (Table 6), shows a slower but similar response to refining. For Pulp 'A', which represents a relatively homogeneous furnish of thin-walled fibres (Figure 12), fibre widths are decreased only slightly by refining. Thus fibre wall mass could also account for the response to refining of fibre width, a conclusion generally confirmed by the data of Table 5.

CONCLUSIONS

Structural organisations of softwood kraft fibres can be very dependent on whether or not they are thick- or thin-walled, or are undried or dried before pulp refining, as well as on pulping, bleaching, and other pulp processing operations.

Undried kraft fibres: Fibre cross-sectional shapes change from being angular to circular, fibre diameters decrease, and walls can delaminate into one or more concentric layers (coarse lamellae) and expand into fibre lumens. Mean cross-sectional wall areas, however, are normally unchanged with pulp refining. Thus, it is concluded that wall material densities of the coarse lamellae of refined fibres could be higher than those of corresponding unrefined and undelaminated fibre walls. Structural elements within the coarse lamellae move relative one to another during refining and become more tightly packed together, numbers and sizes of intra-wall voids created by the dissolution and extraction of wall components during pulping are substantially modified so as to increase wall specific surfaces, wall water-holding capacities, and overall wall substance densities. Kraft fibre diameters decrease with refining due to a tightening and/or lateral contraction of the several spirally oriented lamellae constituting the S1 layer and/or to a decrease in the microfibril angle or lateral contraction of wall lamellae of the S2 layer. During refining it is concluded that structural reorganisation takes place within fibre walls and intra-wall stresses build up to the point where the S2 layer separates or delaminates into one or more concentric layers.

Undried fibres-kraft, soda-AQ, and neutral sulphite-AQ Kraft fibre diameters (widths and thicknesses), wall thicknesses, wall areas, and hemicellulose contents are substantially lower than those of NSAQ and soda-AQ fibres when compared at either the same lignin content or the same pulp yield. The relatively narrow and thin-walled configurations of kraft fibres could be explained by a tightening and contraction of the fibrillar and lamella organisations of the S2 wall layer during pulping. The rate and/ or the extent of removal of hemicelluloses during kraft pulping could possibly also influence final fibre dimensions and properties.

The refining of kraft pulps causes fibre diameters to be decreased further, an effect which could be explained by a further tightening of the fibrillar and lamella wall organisations. Such a response to refining could cause differential stresses to develop within fibre walls resulting in wall delamination and expansion into fibre lumens causing wall thicknesses but not overall wall areas to increase. For soda-AQ pulps, fibre thicknesses decrease with refining but wall thicknesses and wall areas remain unchanged, and walls do not delaminate significantly. The diameters of NSAQ fibres, on the other hand, are unchanged and wall thicknesses, wall areas, and extents of wall delamination increase greatly with refining.

Dried and rewetted fibres Thin- and thick-walled dried and rewetted fibres are collapsed to different extents and can respond to pulp refining in different ways and at different rates. The walls of such fibres are densified by pulp drying processes and in contrast to corresponding undried fibres, are swollen (and delaminated) by pulp refining.

The collapsed configurations of thick-walled, dried and rewetted fibres revert to their uncollapsed state with refining as fibre walls are swollen and intra-wall stresses (developed

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during pulp drying) are released. Thus, pulp refining causes the thicknesses and widths of thick-walled fibres to increase and decrease respectively. For thin-walled fibres, on the other hand, walls are swollen and thicknesses increase, but collapsed configurations are generally retained with pulp refining.

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Transcription of Discussion

EFFECTS OF PULP DRYING AND REFINING ON SOFTWOOD FIBREWALL STRUCTURAL ORGANISATIONS-ADDENDUM

R. Paul Kibblewhite

Effects of refining undried kraft fibres in a PFI mill at 10% stock consistency with an applied load of 1.8 N/mm were monitored. Refining in the PFI mill causes fibre diameters to contract abruptly. This contraction is irreversible and remains with prolonged refining (Figure 1). At the same time actual cross-section fibre wall areas also contract abruptly with refining but these re-expand through wall delamination with prolonged refining (Figure 2).

REFERENCE: KIBBLEWHITE, R.P. - FIBRE AND FIBRE WALL RESPONSE TO REFINING OF SOFTWOOD AND HARDWOOD KRAFT PULPS. (Unpublished Manuscript - In prep. 1989)

EDITOR'S NOTE: This material is additional to that presented in Volume 1 and should be read as part of that paper.

FIGURE 1

THINNINGS/SLABWOOD



FIGURE 2

THINNINGS/SLABWOOD



EFFECTS OF PULP DRYING AND REFINING ON SOFTWOOD FIBREWALL STRUCTURAL ORGANISATIONS-

R. Paul Kibblewhite

Dr. K. Ebeling, James River

Did I understand correctly that when studied under wet conditions the outside diameter of the fibre does not increase in refining, ie. the fibre swells inwards?

Dr. R.P. Kibblewhite

Yes the outside fibre diameter has decreased and for the kraft fibres the wall has gone into the lumen.

Dr. K. Ebeling

Is this under swollen condition or as dried?

Dr. R.P. Kibblewhite

We have solvent exchanged slush, never dried fibres so there is a question mark there. That is why we looked at doing it with Isopropanol and Isopropan - 1 - Pentane. The wall area and volume were greater with that dehydration but the relative difference between the refined and unrefined fibres was the same as we have seen here.

Dr. K. Ebeling

Would you then please explain one of the great accomplishments of this Fundamental Research series, ie. in 1961 when Derek Page and Mr. Tydeman explained the shrinkage of the web during re-drying as being due to the lateral contraction of the swollen cell wall. According to the Page and Tydeman effect the lateral contraction of the cell wall microcompresses axially the fibre below and causes the shrinkage tendency of the web. If you now say that the lateral shrinkage tendency is in the other direction you are then trying to axially extend the underlying fibres. In other words, if you are shrinking during drying from the lumen towards the outer periphery how does the web shrink?

Dr. R.P. Kibblewhite

When we dry these kraft fibres I don't see them doing anything different from what Derek and Tydeman postulated then. We have still got the delaminated wall and I don't see that we have a shrinkage from the lumen end - I don't see we have a problem. Am I misreading you?

Prof. T. Lindstrom, Modo, Sweden

I think we have discussed this topic before Paul. Generally speaking your results cannot be interpreted within the scope of our present understanding. The critical conditions are your dehydration procedures - going from water to acetone, Isopropanol or whatsoever. When you start to beat the fibre you increase the flexibility and it will collapse to a large extent when you change from water to an organic solvent. That could possibly explain your results. It is basically a dehydration effect.

Dr. R.P. Kibblewhite

I would not argue against that one way or the other. We are looking at many different pulps and many different refiners and we are getting very interesting trends and monitoring how the fibres are changing with different types of refiners and pulps. Hardwoods do the opposite they expand with refining. What I am presenting does not, I believe, conflict with the prior art. We overall wall densification, talking about only are not densification of fine lamellae wall elements or aggregates of fine lamellae wall elements.

Dr. G.A. Baum

Paul, did you measure the fibre length change?

Dr. R.P. Kibblewhite

Yes, the length and measurements are available.

Dr. G.A. Baum

Reading your paper and thinking about the S1 layer tightening, one could envision that if you took a fibre that had the S1 layer intact and stretched it out, the fibre diameter could decrease while the fibre cross-sectional area would stay the same. Of course, the lumen would be smaller. you have one of these carnival "finger pulls" and they would cause a decrease in the process.

Dr. R.P. Kibblewhite

When I got all this information and had to come up with an acceptable explanation, a wide range of springs and other models were considered. In any model however changes in microfibril angle needed to be taken into account. Also the cases of a very low microfibril angle where it was basically in the direction of the axis needed to be accounted for. We are not able to measure length closely enough to pick up differences even with the Kajaani.