EVALUATION OF RECYCLING POTENTIAL OF PAPER MAKING FIBERS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, **"EVALUATION OF RECYCLING POTENTIAL OF PAPER MAKING FIBERS"**, in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the Indian Institute of Technology Roorkee, Saharanpur campus, Saharanpur, is an authentic record of my own work carried out during a period from January 1999 to November 2003 under the supervision of Dr. S. P. Singh.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other/Institute/University.

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ABSTRACT

Bagasse and wheat straw are important raw materials for the Indian paper industry, with a potential of high growth. The recycled paper available to the Indian paper industry will have increasing proportions of these fibers in future.

Bagasse and wheat straw are significantly different from woods in terms of fiber morphology and chemical composition. Recycled fibers of these raw materials behave differently from the recycled wood pulps. Recycling potential of the pulps made from these fiber sources is evaluated in the present study.

The thesis consists of six chapters. In the first chapter, the need and aim of the work have been described. A brief introduction of the methodology adopted and the scope and limitation of the study have been discussed.

Chapter 2 covers a review of the available literature in this area. The effect of recycling on different properties of wood pulps has been extensively studied. It is evident that the most detrimental effect of recycling on papermaking fibers is loss in tensile strength. Several mechanisms have been put forth to explain this loss based on studies of physical and chemical changes that take place in the fiber during recycling. The generally accepted view is that the loss in tensile strength is due to loss of fiber swelling on drying of pulps. The loss in fiber swelling reduces the mobility of surface molecules, this in turn decreases inter molecular interaction between two fiber interfaces resulting in a decrease in fiber-fiber bond strength. The relative bonded area decreases for stiffer recycled fibers. The recycling potential of fibers sourced from a given raw material depends on the yield of pulp. The amount of hemicelluloses present in pulp has been found to play an important role in the pulp's recycling potential. Refining of recycled pulps increases both tensile strength and fiber swelling but at the cost of increased drainage resistance. The problems of slow drainage of recycled pulps can be alleviated to some extent by techniques such as fractionation, addition of strength aid, and enzyme treatment of recycled pulps.

Chapter 3 describes the pulps used for the recycling experiments. Single specie pulps of bagasse and wheat straw, three chemical pulps and two semichemical pulps, were prepared in the laboratory. A commercial chemimechanical of bagasse was procured from a large Indian newsprint mill.

Chapter 4 presents the details of experimental work on recycling of pulps. The pulps were subjected to six cycles of sheet making – drying – reslushing. Various properties of the pulps were evaluated for the standard handsheets prepared at different cycles. No chemical or mechanical treatment was given to the pulp between the cycles. The wheat straw pulps have shown a higher recycling potential than the bagasse pulps. The loss in strength of bagasse pulp is of the order of the loss reported for wood pulps. Fiber classification remains nearly unchanged on recycling of wheat straw pulps, but shows a high loss of fines (P200) fraction on recycling of bagasse pulps. There appears no major impact of recycling on the fiber length. The proportions of alpha-, beta-, and gamma-cellulose do not change with recycling of bagasse and wheat straw pulps. However, the bagasse pulp with lower gamma cellulose content than the wheat straw pulp suffered a greater loss in tensile strength.

Chapter 5 describes the experimental work to study the response of conventional strength enhancement treatments of recycled pulps. The recycled pulps were subjected to alkali treatment, refining, and combination of both. For some experiments, the pulps were fractionated into a fine and coarser fractions, and the coarser fraction was refined separately and mixed back with the fines. Physical and strength properties of the treated pulp have been compared with the properties in untreated recycled and virgin state. Freeness of the recycled pulps decreases sharply on refining. Reduction in freeness due to refining is more severe for wheat straw pulps. Very fine particles (P250) contribute to a great deal in the slowness of the wheat straw pulp, as indicated by a significant rise in freeness when this fraction was removed from the pulp.

Chapter 6 summarizes the main conclusions and the recommendations for the future work.

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Glossary

AKD – Alkyl ketene dimer
BCMP – Bagasse chemimechanical pulp
BCP56 – Bagasse chemical bleached pulp of 56% unbleached yield
BK – Bleached kraft pulp
BMC – Bauer-McNett classifier
BS – Bleached sulfite pulp
BSP65 – Bagasse semichemical pulp of 65% yield
CEDED – Bleaching sequence
CEH – Bleaching sequence
CEHH – Bleaching sequence
Ch – Change
CMP – Chemimechanical pulp
CSF – Canadian Standard freeness
CTMP – Chemithermomechanical pulp
DP – Degree of polymerization
EP – Eastern pine
ES – Eastern spruce
FMP – Fractionated mixed pulp, refined R48 fiber fraction and fines fractions Mixed in 1:1 ratio
o.d. – Oven dried
FSP – Fiber saturation point
HFP – High freeness pulps
HSF – High shear force
HW – Hardwood
HYSP – High yield sulfite pulp
LFP – Low freeness pulps
NMR – Nuclear Magnetic Resonance spectroscopy
NP – Northern pine
NSW – Northern softwood
OCC – Old corrugated containers
P200 – Fiber fraction that passed 200-mesh of Bauer-McNett classifier

P48/R250 –	Fines fraction, fraction that passed 48- mesh and retained on250-mesh synthetic cloth
Ref_R48 –	R48 fiber fraction refined in a PFI mill for 3500 revolutions
PS –	Print-surf
R100 –	Fiber fraction retained on 100-mesh of Bauer-McNett classifier
R48 –	Fiber fraction retained on 48-mesh of Bauer-McNett classifier
RBA –	Relative bonded area
RS –	Rosin sizied
SGW –	Stone ground wood pulp
SP –	Southern pine
SW –	Softwood
T – S –	Tensile index versus scattering coefficient
TEA –	Tensile energy absorption
TEM –	Transmission electron microscopy
TMP –	Thermomechanical pulp
UBK –	Unbleached kraft pulp
WC –	West Coast
WCP42 –	Wheat straw chemical bleached pulp of 42% unbleached yield
WCP49 –	Wheat straw chemical bleached pulp of 49% unbleached yield
WRV –	Water retention value
WS –	Wheat straw
WSCP60 –	Wheat straw semichemical pulp of 60% yield
ZSTI –	Zero-span tensile index
ZSTS –	Zero-span tensile strength

CHAPTER 1

INTRODUCTION

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INTRODUCTION

1.1 BACKGROUND

Recycled fibers have established themselves as a potential raw material for paper industry globally. The use of recycled fibers in manufacture of paper is both economical and environment friendly. Recycled fibers help in reducing deforestation, consumption of energy and chemicals for pulping and bleaching, formation of toxic byproducts during pulping and bleaching, consumption of water, and cost of treatment of effluents. In the recent past, the annual increase in the consumption of secondary fiber has been about 6% in contrast to an annual growth of about 2% in the consumption of virgin pulp. Currently, about 48% of the paper and paperboard produced globally is based on the recycled fiber (1).

The recycled fiber plays a much more important role for the Indian paper industry for several reasons. India is a fairly small player in the global paper industry with an installed paper manufacturing capacity of only 7.4 million tons per annum compared with 330 million tons per annum of the world (1,2). The Indian paper industry should grow rapidly consistent with its present high economic growth rate. A growth rate in paper consumption in India is projected to be 10% (3). As there is a shortage of supplies of forest-based fiber to the Indian paper industry, new capacities are expected to be based primarily on agricultural residues and wastepaper.

The present installed capacity of 7.4 million tons per year can be divided into three categories namely; wood based – 3.5 million tons per year, agro based 1.9 million ton per year and wastepaper based – 2.0 million tons per year (2,4). As mentioned earlier, more of agricultural residues and wastepaper will be used in paper production in future. Consequently, the recycled paper available to the Indian paper industry will have a higher proportion of agricultural residue fiber.

A large body of research output is available covering different aspects of paper recycling. Many research projects are still underway throughout the world. Recycling studies reported in literature can be broadly divided into four categories:

1. Problems related to collection and sorting of wastepaper for different grades of paper to be made.
2. Removal of contaminants by screening, cleaning, and/or deinking.
3. Study of changes in fiber characteristics on its repeated use in papermaking.
4. Response of recycled fiber to refining and other techniques of fiber quality enhancement.

Studies in the third and fourth categories reported so far are largely based on wood pulps, especially softwood pulps. Few references are available on the recycling potential of nonwood pulps. Bagasse and wheat straw are the major nonwood raw materials used by the Indian industry, with a potential of high growth. Therefore, there is a need to study the recycling potential of the pulps made from these fiber sources. Both, bagasse and wheat straw are significantly different from woods, in terms of fiber morphology and chemical composition (Table-1.1).

The hemicelluloses present in softwoods contain a very high proportion of mannan along with xylan, while the hemicelluloses in agricultural residues are mostly xylan and the mannan is nearly absent. It is suggested in the literature that the recycling potential of pulps is influenced by nature of hemicelluloses present in them. The pulps with high xylan content have a high recycling potential (7). Mixing of wheat straw and softwood kraft pulps in a 30:70 ratio is reported to increase the

Table- 1.1: Chemical composition of papermaking raw materials.

Type	Region	Ash (%)	Lignin (%)	Cellu-lose (%)	Hemicell-ulose (%)	Glucan (%)	Galac-tan (%)	Man-nan (%)	Aran-ban (%)	Xylan (%)
Softwoods (5)										
East. Hemlock	N. American	0.2	32.5	42	26	45.3	1.2	11.2	0.6	4.0
Jack pine	N. American	0.2	28.6	41	30	45.6	1.4	10.6	1.4	7.1
White spruce	N. American	0.3	27.1	44	29	46.5	1.2	11.6	1.6	6.8
Spruce	Scandinavian	0.4	28.6	43	27	44.3	1.9	10.3	0.5	7.6
Pine	Scandinavian	0.4	27.8	44	26	44.8	1.3	7.6	0.6	7.2
Hardwoods (5)										
Aspen	N. American	0.2	16.0	53	31	57.3	0.8	2.3	0.4	16.0
Beech	N. American	0.4	22.1	42	27	47.5	1.2	2.1	0.5	17.5
White birch	N. American	0.2	18.9	41	40	44.7	0.6	1.5	0.5	24.6
Yellow birch	N. American	0.3	21.3	40	39	46.7	0.9	3.6	0.6	20.1
Birch	Scandinavian	0.3	19.5	40	39	37.5	1.0	0.5	0.5	24.6
Non woods										
Wheat straw (5)		1.6	22.0	42	36	44.8	0.9	-	2.0	22.6
Wheat straw (6)		4.5-9	16-21	29-51	26-32	-	-	-	-	-
Bagasse (6)		-	-	-	-	47.4	-	-	1.7	27.6
Bagasse (6)		1.5-5	19-24	32-48	27-32	-	-	-	-	-

recycling potential of softwood pulp due to an increase in the xylan content of mixture (8).

1.2 STATEMENT OF THE PROBLEM

The aim of the present study is to evaluate the recycling potential of bagasse and wheat straw pulps at different yields, commonly used by the Indian paper industry. The attempt is made to provide answers to three basic questions: 1) What is the effect of recycling on the sheet structure and strength properties? 2) How do the recycled pulps respond to strength enhancement methods commonly employed for recycled pulps? 3) How does the recycling behaviour of these pulps compare with the wood pulps?

1.3 OBJECTIVES

The objectives of present work may be summarized as:

1. To assess the effect of changes that occurs in and on fiber during recycling of bagasse and wheat straw pulps.
2. To assess the effect of treatments, usually employed for enhancement of strength properties on recycled pulps of bagasse and wheat straw.
3. To search and analyze the reasons of strength loss on recycling of pulps.

1.4 METHODOLOGY

1. Several types of raw materials are used in Indian mills, and there is a tendency of mixing all the pulps in the blow tank for further processing. Under the present mill practices, it is difficult to obtain commercial pulps from a single raw material. Therefore, single specie pulps of bagasse and wheat straw were prepared in the laboratory. Three chemical and two semichemical pulps were made. A

commercial chemimechanical pulp (CMP) of bagasse from a large Indian newsprint mill was also included in the study.

2. Experimental methods used in the recycling studies reported have been many and varied. Laboratory handsheet machines for sheet formation have been used in many studies. In the experiments reported in literature, the pulps have been subjected to varying refining, pressing and drying conditions between the cycles. In some cases, sizing chemicals were also added between the cycles.

   In the present study, the pulps were subjected to six cycles of sheet making – drying – reslushing. No chemical or mechanical treatment was given to the pulp between the cycles, except when these treatments were studied as possible methods of quality enhancement of recycled fibers.

3. The initial freeness of the pulps used for recycling study was kept in the range of 350 to 300 ml CSF. Chemical pulps were beaten in a valley beater to achieve the desired freeness. Semichemical pulps were obtained by refining to the desired freeness in a laboratory sprout waldron refiner. Standard handsheets were prepared for evaluation of various properties from a portion of the pulp. From the remaining portion, thick pads (350 – 450 g/m^2) were prepared on the same sheet-making machine to speed up the experimental work. The pads were wet pressed (700 kN/m^2) and dried on a cylinder heated to 80°C in contact with gloss plates. For the subsequent cycles the pads were reslushed and remade into handsheets and pads.

4. For some cycles, recycled bleached chemical pulps of bagasse and wheat straw were subjected to commonly employed strength enhancement techniques. These included: a) refining, b) alkali treatment, c) alkali treatment followed by

refining, and d) classification of recycled pulp into long fiber and fines fractions, separately refining the long fiber fraction, and remixing the two fractions.

5. Evaluation of handsheets for various strength and physical properties and analyzing the data in the light of available knowledge in this field.

1.5 SCOPE

The results of this study suggest that the agricultural residue pulps, especially wheat straw pulps, loose much less strength on recycling than wood pulps. The results will be useful for evolving suitable strategies for increasing usage of recycled fiber, especially from bagasse and wheat straw, in the manufacture of different grades of paper.

1.6 LIMITATIONS

In the present study, all the recycling experiments, from pulp making to sheet making have been conducted in laboratory. The mill conditions differ from the laboratory conditions at almost each step. Further, the recycled sheets in these experiments were not subjected to those operations to which actual paper goes through during printing, converting, and end-use. These conditions may influence the recycling behaviour of the paper.

CHAPTER 2

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Chapter 2

LITERATURE REVIEW

Loss of strength properties or changes in the other properties of the paper made from the recycled pulp is widely studied by various investigators (7-29). A large volume of literature is available on the evaluation of recycling potential of fibers, mainly prepared by softwoods. These results have been thoroughly reviewed by many (22,30-34). In this review we have tried to update some of the recent findings.

2.1 EFFECT OF RECYCLING ON PULP PROPERTIES

2.1.1 FIBER DIMENSIONS

Drying-rewetting cycles on pulps do not produce any noticeable change in fiber length even after four or six cycles (18,20,22,24,25,29,35). This is true for both chemical and mechanical pulps. Any mechanical action on recycled fibers, e.g. refining, causes severe fiber shortening and increases the fines percentage in the recycled pulp (14,36,37). Even the calendaring of paper made from recycled fiber is reported to increase fines content in the next cycle (14).

Drying-rewetting cycles cause a slight decrease in fiber perimeter (22,25), possibly due to fiber wall shrinkage. Jang et al. (25) found about 8% decrease after five cycles in fiber wall cross sectional area for TMP, CTMP and kraft pulp. The effect of recycling on fiber coarseness, weight per unit length of fiber (mg/100m), is also negligible (21,22,24,35). However, if the fibers are subjected to mechanical actions between the cycles, the fiber coarseness is found to decrease. Eriksson et al. (29) observed a decrease in fiber coarseness of TMP fibers when printing and deinking steps were also included in the recycling experiments.

2.1.2 PULP FREENESS

Several authors have reported that drying-rewetting cycles increase the freeness of chemical pulps (11,13,16), as well as mechanical pulps (27,28,29). In contrast with these observations, Howard and Bichard (20) observed a decrease in freeness with recycling for eleven chemical and mechanical pulps. The effect of recycling on pulp freeness appears to depend on the initial freeness of the pulp. Law et al. (28) observed that on recycling the freeness decreased for low initial freeness pulps and increased for high initial freeness pulps. They observed further that when the pulp was fractionated into long fibers and fines, the freeness of long-fiber fraction increased and of fine fraction decreased with recycling. Bobalek and Chaturvedi (18) found insignificant changes in freeness on recycling of lightly beaten pulps.

2.1.3 APPARENT DENSITY, AIR RESISTANCE AND SCATTERING COEFFICIENT

The apparent sheet density of low-yield chemical pulps is found to decrease on recycling (11,12,14,20,24). A 10% to 20 % reduction is normally observed for five to six recycles. For high-yield mechanical pulps, the sheet density increases on recycling (20,17,28,29). For chemimechanical and other intermediate yield pulps, the recycling has only a small effect on the apparent sheet density (27). The sheet density is related with the fiber-fiber bonding. Apparently, the pulp that produces strong interfiber bonds in its virgin state looses its bonding ability on recycling, and gives a low-density sheet. On the other hand, the pulp that produces weak bonds in first cycle shows an increase or no change in its bonding ability on recycling. This is in agreement with the observation of Bobalek and Chaturvedi (18) who found insignificant changes in density for lightly beaten chemical pulps.

The effect of recycling on air-resistance, as measured by Gurley method, follows the same trend as the apparent density. Chemical pulps exhibit decrease in air resistance on recycling as they show a decrease in apparent density.

In recycling experiments, the scattering coefficient is measured to estimate the relative bonded area. In general, for chemical pulps the scattering coefficient increases indicating a decrease in bonding properties and thus, loss in tensile strength (20,22,35,41).

2.1.4 STRENGTH

Recycling has a major effect on strength properties of pulp. Chemical pulps show a different behaviour from mechanical pulps as shown in Fig. 2.1 (20).

On recycling of chemical pulps the tensile strength decreases significantly, whereas for mechanical pulps, the change in tensile strength is less significant but it is in upward direction in most cases. The chemimechanical and semichemical pulps show behaviour intermediate between chemical and mechanical pulps. Some of the experimental results on various furnishes are summarized in the Table- 2.1 (page 12). The loss in tensile strength of chemical pulp has been reported between 20% and 70% depending upon the type of raw material, conditions of pulping and bleaching, and the recycling procedures adopted. The main reason for the loss in tensile strength of recycled fibers is reduced fiber-fiber bonding. For mechanical pulps, however, the recycling increases the fiber flexibility and fiber bonding.

Recycling affects the burst strength in a similar way as it affects the tensile strength. The data of Table- 2.1 (page 12) indicate that the changes on recycling in burst and tensile strength follow the same trend.

The effect of recycling on tear strength of pulp is not as well defined as for tensile strength as evident from the data of Table- 2.1 (page 12). However, in most cases the tear strength on recycling increases for chemical pulps and decreases for mechanical pulps. Several authors (20,28,29) have reported that there is no change in the tear strength after many cycles. Chatterjee et al. (21) explained some of these discrepancies by recalling that the tear strength passed through a maximum on a beating curve. The reduced fiber bonding due to recycling of chemical pulp would result in decrease or increase in tensile index depending on

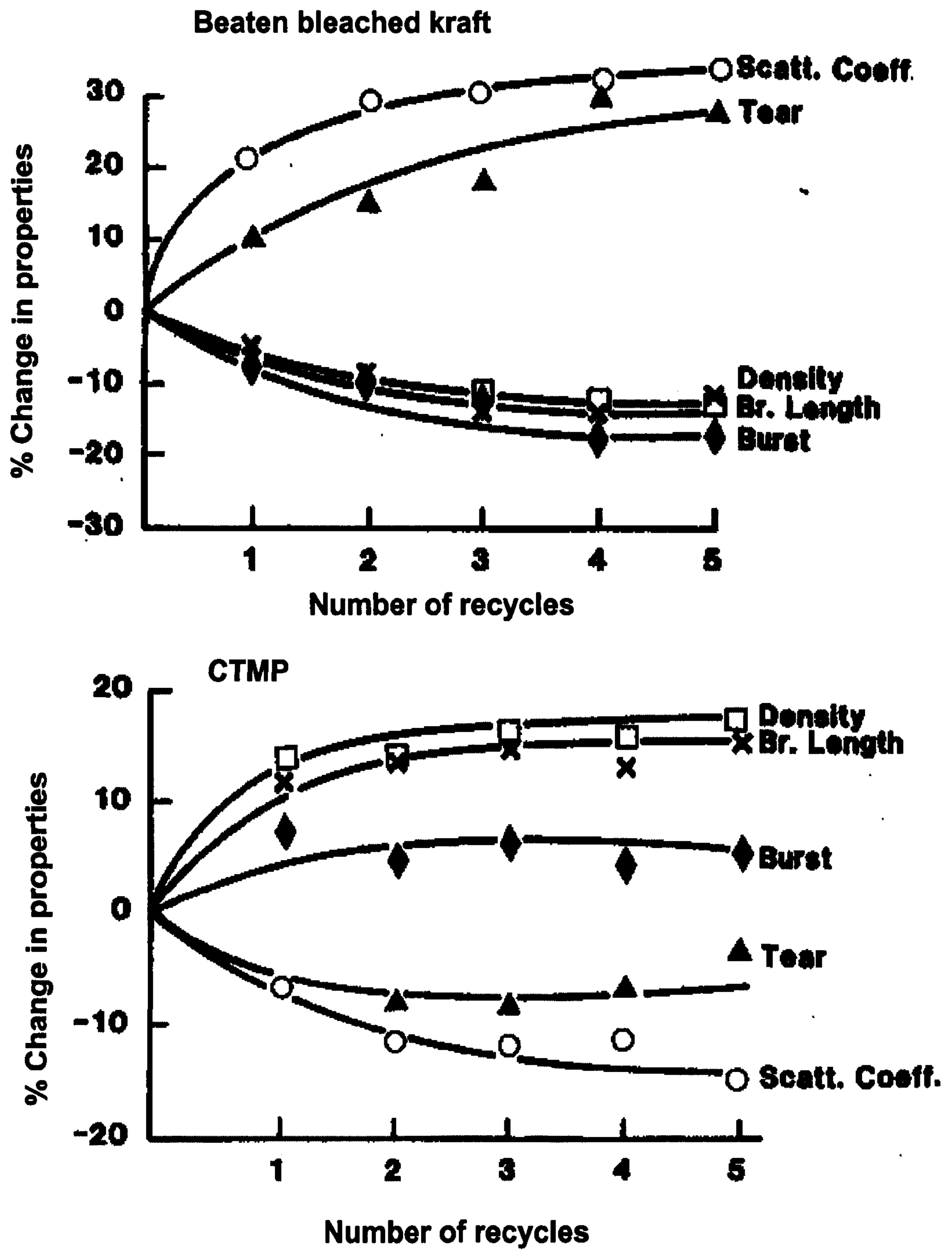

Fig. 2.1: The percentage in sheet properties during recycling of beaten bleached kraft pulp and CTMP. (Ref. 20)

Table- 2.1: Strength loss reported by various investigators for wood pulps.

Authors	Furnish/CSF or °SR	Tensile Strength	Burst Strength	Tear Strength
R.C. Mckee (11)	UBK /325 ml	↓ II-6%, VII-29%	↓ II-14%, VII-38%	↑ II-6%, VII-24%
	BK /600 ml	↓ II-21%	↓ II-19%	↑ II-25%
	BK /450 ml	↓ II-30%	↓ II-28%	↑ II-35%
	BK /300 ml	↓ II-34%	↓ II-36%	↑ II-40%
	SGW /110 ml	↓ II-11%	↓ II-5%	↓ II-9%
Bovin, Hartler & Teder (12)	UBK /30 °SR	↓ II-23%, VII-58%	-	↑ II-29%, VII-68%
	UBS /30 °SR	↓ II-29%, VII-53%	-	↑ II-25%, VII-38%
	BS /30 °SR	↓ II-22%, VII-75%	-	-
	Mech. Pulp /52 °SR	No change	-	No change
Cildri & Hwarth (13)	BS /37 °SR	↓ II-35%	-	↓ II-45%, V-35%
Hron (14)	UBK, SP /270 ml	↓ II-34%, V-48%	↓ II-40%, V-77%	↑ II-33%,↓ V-16%
	UBK, SP, RS /285 ml	↓ II-44%, V-74%	↓ II-31%, V-50%	↑ II-23%,↓ V-12%
	BK, NSW, RS /285 ml	↓ II-44%, V-78%	↓ II-43%, V-80%	↑ II-9%,↓ V-20%
Pycraft & Howarth (15)	BS /47 °SR	↓ II-11%, V-14%	-	-
Yamagishi & Oye (16)	BK, HW /343 ml	↓ II-60%, VI-70%	-	↓ II-24%, VI-37%
	BK, SW /326 ml	↓ II-49%, V-58%	-	↑ II-78%, VI-100%
Klungness & Caulfield (Unbeaten pulp) (17)	UBK, (60% yield)	↓ 53%	↓ 52%	↓ 25%
	UBK, (46% yield)	↓ 24%	↓ 17%	↑ 12.5%
	BK, CEDED	↓ 31%	↓ 37%	↑ 7%
Bobalek & Chaturvedi (18)	BK, SP /500 ml	↓ II-17%, V-37%	-	-
	BK, Eucaly. /450 ml	↓ II-17%, V-30%	-	-
	BK, NP /600 ml	↓ II-0%, V-19%	-	-
	BK, Aspen /550 ml	↑ II-6%,↓V-6%	-	-
Howard & Bichard (20)	SGW /236ml	↑ II-6%, VI-11%	↑ II-2%, VI- 0%	Insignificant Ch
	TMP /83ml	↑ II-4%, VI-28%	↑ II-5%, VI-27%	Insignificant Ch
	CTMP /80ml	↑ II-12%, VI-15%	↑ II-7%, VI-18%	↓ II-9%, VI-3%
	BS, ES+EP /255 ml	↓ II-15%, VI-11%	↓ II-15%, VI-17%	↑ II-10%, VI-14%
	BK, WC /180ml	↓ II-13, VI-15%	↓ II-11%, VI-19%	↑ II-9%, VI-21%
	BK, ES /246 ml	↓ II-5%, VI-24%	↓ II-7%, VI-21%	↑ II-10%, VI-28%
Chatterjee et al. (21)	UBK, Spruce /688 ml	-	-	↑ II-20%,↓ V-27%
	HYSP, Spruce /435 ml	-	-	↑ II-2%, V-8%
	TMP, Spruce /142 ml	-	-	↑ II-2%,↓ V-8%
Eills & Sedlachek (22)	UBK, Pine	Decreases	-	-
	BK, Pine	Decreases	-	-
	UBK, HW	Decreases	-	-
	BK, HW	Decreases	-	-
Gratton (23)	TMP, (One cycle)	Insignificant Ch	Insignificant Ch	Increases
Klofta & Miller (24)	BK, SW+HW /480 ml	↓ II-2.4%, V-43%	-	-
Law et al. (27)	TMP, Spruce	No change	No change	Increases
	Eight CMPs, Aspen	Small ↓	Small ↓	Slight Increase
Law, et al. (28)	TMPs, Pine & Spruce	LFP ↑, HFP ↓	LFP ↑, HFP ↓	LFP ↑, HFP ↓
Ericksson et al (29)	TMP /102 ml	↓ II-11%, V-13%	-	Insignificant Ch
Cao et al. (7)	Pulps of Diff. lignin & pentosans contents	↓ For all	↓ For all	↑ For all
Aravamuthar & Greaves (8)	UBK, SW	↓ II-13%, V-38%	↓ II-19%, V-48%	↓ II-3%, V-4%
	UBK, SW+WS, 30:70	↓ II-6%, V-30%	↓ II-13%, V-35%	↑ II-10%, V-4%

Glossary

BK – Bleached kraft pulp
BS – Bleached sulfite pulp
CEDED – Bleaching sequence
Ch – Change
CMP – Chemimechanical pulp
CTMP – Chemithermomechanical pulp
EP – Eastern pine
ES – Eastern spruce
HFP – High freeness pulps
HW – Hardwood
HYSP – High yield sulfite pulp
LFP – Low freeness pulps
NP – Northern pine
NSW – Northern softwood
RS – Rosin Sizied
SP – Southern pine
SWG – Stone Ground Wood
SW – Softwood
TMP – Thermomechanical pulp
UBK – Unbleached kraft pulp
WC – West Coast
WS – Wheat straw
↑ – Increase
↓ – Decrease

whether the pulp in its virgin state was beaten to exceed the maximum in tear curve or not.

Tear strength of a paper sheet is a complex function of fiber properties and the degree of sheet consolidation (38,39). Among all the factors, the fiber length has the greatest influence on the tear strength. The longer the fiber the greater is the tear index. However, the degree of dependence of tear on fiber length is influenced largely by fiber bonding. For a well-bonded sheet of paper the dependence of tearing resistance on fiber length decreases and the role of fiber strength becomes predominant (38). This implies that the tear strength should increase with the decrease in fiber bonding if the fiber length is held constant.

2.2 MECHANISMS OF STRENGTH LOSS

The loss of strength of pulp on recycling has been attributed to several factors. Some of these factors are: change in chemical composition of the fiber, the loss in fiber strength, the degradation of cellulose, and the loss in fiber bonding due to hornification. The changes in chemical composition and fiber strength are of relatively small magnitude. Significant losses in the tensile strength observed during recycling cannot be due to the minor loss in fiber strength. Loss in relative bonded area and bond strength between fibers due to stiffening and hornification of fibers seem to be the main factors responsible for loss in strength properties on recycling of pulps. Major findings of these aspects have been briefly reviewed in the following paragraphs.

2.2.1 SHEET STRENGTH - THEORETICAL BACKGROUND

The strength of a paper sheet is governed by the strength of the fibers forming the sheet and the strength of the bonds between the fibers. Page (40) expressed this relationship in the so called Page equation. The equation is as follows:

$$\frac{1}{T}=\frac{9}{8Z}+\frac{12C}{PLb(RBA)} \qquad (2.1)$$

Where T is tensile strength of paper, Z is zero-span tensile strength, b is bond strength, RBA is relative bonded area, L is fibers length, C is fiber coarseness, and P is perimeter of fiber. For weakly bonded sheet, the fiber bonding expressed as the second term in Eq. 2.1 controls the overall strength of the sheet. As the bonding strength between the fibers increases, the sheet rupture is caused by the breaking of the bonds as well the breaking of the fibers. For highly bonded sheet, the fiber strength, expressed as the first term in Eq. 2.1 controls the overall strength of the sheet.

Cildir and Howarth (13) and, Pycraft and Howarth (15) in their studies found that the loss in tensile strength of paper on recycling was mainly due to the loss in the bonding strength, whereas the loss in the fiber strength was either very small or insignificant. Eills and Sedlacheck (22) studied the effect of recycling on the variables in the second term of the page equation. They rearranged the Eq. 2.1 in the form given in Eq. 2.2:

$$\left[\frac{1}{T}-\frac{9}{8Z}\right]^{-1}=\frac{b}{k}-\left[\frac{b}{kS_0}\right]S \qquad (2.2)$$

Where $$RBA=\frac{S_0-S}{S_0}$$

S_0 = the scattering coefficient of a sheet of unbonded fibers

S = the scattering coefficient of the paper

$$k=\frac{12C}{PL}$$

The term on the left hand side of Eq. 2.2 has been named as 'Page bonding strength index'. When the Page index was plotted as a function of scattering coefficient of paper sheet, a common straight line resulted for virgin as well as recycled pulps. It was concluded that the bond strength, b, remained constant on recycling of pulp, as k was found to be constant from independent measurements of P, C, and L. Therefore the loss in sheet strength was due to a reduction in the relative bonded area only.

In contrast, Page et al. (35) found that the primary cause of tensile strength reduction upon drying was the loss of shear bond strength rather than the relative bonded area. This difference of opinion arises on the use of Page equation. Seth & Page (41) indicated that the Page equation might not be used to estimate loss of shear bond strength during drying and rewetting cycle, since some of the basic assumptions in deriving the equation may not hold good. They suggested that the equation could be used if different experiments gave the same sheet elastic modulus at same bonded area. They also found that the sheet modulus of elasticity decreased appreciably at a given bonded area upon drying.

Elastic modulus of a paper sheet will depend on the curls, crimps and kinks in the fiber. A fiber segment with a crimp or kink would have a lower elastic modulus than a straighter segment, and would be unable to take full load in a network under strain resulting in nonuniform stress distribution (42,43,44). Another factor that influences elastic modulus of a paper sheet is the shrinkage potential of the fibers. Shrinkage potential increases with fiber swelling and fines (45). At high levels of shrinkage elastic modulus is inversely proportional to the drying shrinkage that was allowed. Lower shrinkage potential of once dried fibers, due to loss of swelling potential, may also be a possible reason for loss of sheet elastic modulus and sheet tensile strength at a given fiber length and relative bonded area.

Page et al. (35), in their experiments, recycled only long fiber fraction (R14) eliminating the impact of fines, and observed that the fiber curl did not increase in drying and rewetting cycles. The relationship between elastic modulus and scattering coefficient remained unchanged and the Page equation could be used for estimation of shear bond strength. It was observed that the major portion of loss in the Page bonding strength index upon drying was due to the loss of shear bond strength than loss of bonded area, as shown in Fig 2.2.

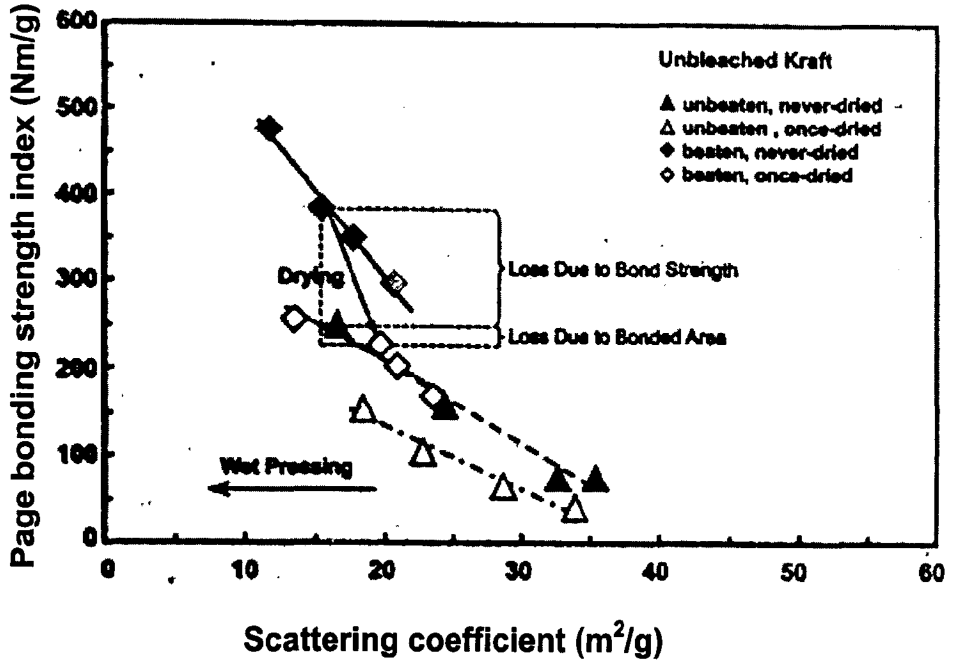

Fig. 2.2: The Page bonding strength index is plotted as a function of the scattering coefficient. Drying reduces the shear bond strength of paper by 30% for unbeaten pulp and by 46% for beaten pulp. (Ref. 35)

The mechanism to account for the decrease in shear bond strength upon drying is not fully clear (35). It could be surface changes at the fibrillar or the molecular level. If surface changes at molecular level are considered, then the loss in bond strength can be explained on the basis of the diffusion theory of adhesion used by Mckenzie (46) and Clark (47). According to the diffusion theory adhesion between plasticized polymeric materials will occur as a result of significant intermingling of molecular segments from both sides of the interface. Clark and Mckenzie have related the presence of mobile chains or molecules on the fiber surface to the shear bond strength. Page et al. (35) have speculated that the mobility of surface molecules is reduced due to loss of fiber swelling on drying, this is turn decreases inter molecular interaction between two fiber interfaces resulting in a decrease in fiber-fiber bond strength.

2.2.2 CHANGE IN CHEMICAL COMPOSITION

The effect of recycling on chemical nature of pulp has been a subject of a few studies. Many authors have suggested that hemicelluloses play an important role in fiber bonding. The presence of accessible hemicellulose on fiber surface, and their abundance in the cell wall, enhances both fiber bonding and flexibility of the wet fibers. Hemicelluloses precipitate on the pulp fiber surface in the final stages of alkaline cooking and during refining and improve the paper forming properties of fibers. Any loss of hemicelluloses from the fiber surface would cause deactivation of fiber surfaces (32). Eastwood & Clarke (48) observed solubilization of a small portion of pentosans from a beaten semi-bleached kraft pulp after recycling three times. They speculated that this loss of pentosans content was related with the loss of fiber flexibility and the surface conditions of the fiber.

However, after a thorough study on the changes due to recycling in chemical properties of a variety of pulps, Bouchard and Douek (25) have concluded that the chemical analysis of fibers could not differentiate between virgin and recycled fibers in a paper furnish. The loss in strength properties on recycling is related more with physical changes in the fiber rather than the small chemical changes. Their results are summarized in the following paragraph;

The concentration of lignin remains essentially unchanged at various stages of recycling. The loss of pentosan content is limited to $\approx$ 1.5% after five cycles in beaten unbleached kraft pulps. There is no direct correlation between the dissolution of pentosans and lignin to changes in strength properties during recycling.

2.2.3 CELLULOSE DEGRADATION

Pulp viscosity, a common measure of degree of polymerization (DP) of cellulose molecules, has been reported to be influenced by the recycling of pulp. Oye and Yamagishi (16) observed a decrease in pulp viscosity on recycling of bleached kraft pulps, when the sheets were dried at 80°C between the cycles. Klungness and Caulfield (17) dried the pulp sheets at 140°C and observed that the drying had only a minor effect (less then 7%) on the viscosity of the unbleached pulps, but a significant effect (31% decrease) on the viscosity of bleached pulp.

Bouchard and Douek (25) observed that recycling of kraft pulp caused a partial depolymerization of cellulose. The longer cellulosic chains were more sensitive towards depolymerization possibly due to the mechanical action or stress imposed on the fiber during the sequence of drying and rewetting. The loss in pulp viscosity due to recycling has not been found in correlation with loss in sheet strength.

Paper made in acidic conditions causes hydrolysis of cellulose. Acid penetrates the open amorphous regions of the fiber and cut the C–O glycosidic bonds that link glucose units in the cellulose chain. Oxidation of cellulose unit can break C–H bonds, as well as C–O bonds. This reduces the degree of polymerization and makes the fiber more fragile and susceptible to breakage during subsequent refining (49,50). Higher losses observed by Horn (14) in zero-span tensile strength on recycling of handsheets sized with rosin-alum, may be due to degradation of fiber under acidic conditions.

Stockman and Teder (51) studied the effect of drying temperature on the degree of polymerization (DP) of different chemical pulps. They observed that the DP of chemical pulps on heating in range of 70°C to 140°C did not change significantly. The bleached Kraft pulp however was very sensitive to temperature exceeding 140°C. It may be concluded that change in fiber strength on recycling depends upon the type of pulp, refining conditions and drying temperature in the initial cycle.

2.2.4 ZERO-SPAN TENSILE STRENGTH

The loss in fiber strength on recycling of pulp has been studied in terms of zero-span tensile strength. It appears from the literature that the effect of recycling on zero-span tensile strength is unpredictable. This difference in observations may be because the experimental conditions used by different workers were different. Many workers (20,21,24) have found that zero-span tensile strength remains unchanged during recycling of chemical pulps, while many others (11,14,21,22) have observed a reduction in zero-span tensile strength.

Klofta and Miller (24) found no change in the zero-span tensile index on recycling bleached kraft pulp (70%HW, 30%SW). The pulp was beaten to 480ml CSF before recycling, and the sheets were dried at 108°C under restrained conditions. Howard and Bichard (20) found no change in dry and wet zero span tensile strength during recycling for both chemical and mechanical pulps even after six cycles. The sheets were air-dried between the recycles.

Mckee (11) observed 22% fall in zero-span tensile strength after six cycles for unbleached kraft pulp. The pulp was initially beaten to 325 ml CSF. Sheets were dried using steam-heated dryer and the recycled pulp was beaten to 325 ml CSF between the cycles. Horn (14), after five cycles, observed 17% fall in zero-span tensile strength for unsized sheets of unbleached southern pine kraft pulp. When one percent rosin size was added to the same stock, the loss in zero-span tensile strength after five cycles was found to be 33%. For rosin-sized sheets of bleached northern pine pulp, the loss in zero-span tensile strength, after five cycles, was

51%. The sheets were dried on steam-heated cylinders and calendered after drying.

Bobalek and Chaturvedi (18) showed increase in zero-span tensile strength on recycling of softwood and hardwood bleached kraft pulps. In the experiments of Bobalek and Chaturvedi, the pulp was only lightly beaten initially and the sheets formed between the cycles were air dried without wet pressing.

For mechanical pulps the literature suggests that there is either no change or slight increase (11,20,21,27) in the zero-span tensile strength on recycling.

2.2.5 HORNIFICATION

The largest changes in properties of paper made from recycled pulp are observed due to repeated wetting-drying cycles. The structural changes that take place in the cell wall of fiber from a drying -and- rewetting cycle are commonly referred to as hornification. The term was used by Jayme (52) for the first time in 1944. Hornification is associated with the loss of swelling of the fiber wall, and a stiffening of the fibers that reduces their ability to form inter-fiber bonds. Hornification, especially for low yield chemical pulps, is an irreversible process. Several researchers have found that the extent of swelling for recycled fibers would not be achieved as that of virgin fiber even after prolonged soaking of the pulp (9,10).

Cell wall of fiber consists of several lamellae of cellulose fibrils. During drying, as the water leaves lamellae, high surface tension forces draw them closer together forcing the lamellae adhere to one another. The situation is not entirely reversed on rewetting, resulting reduction in fiber swelling. This is very pronounced in chemical pulps and reduces the fiber flexibility (19).

Measure of Fiber Swelling

Two methods are commonly employed for measurement of ability of fiber to swell; water retention value (WRV) and fiber saturation point (FSP). Jayme (52) developed the method for determination of WRV. In this method, a wet pulp sample is subject to a centrifugal force for a specified time, after which it is weighed, dried and reweighed and its water content determined (10,53). The water retention value (WRV) is obtained by expressing the water content as a percentage of the dry weight of pulp.

Another method of measuring swelling and examining the internal structure of water swollen fiber wall is based on the work of Stone and Scallan (54). Using a solute exclusion technique with a macromolecule so large as to be totally excluded from entering even the largest pores in the wall, they were able to determine the total amount of water in the porous structure of the fiber walls. This total amount of water in the pores is termed the fiber saturation point (FSP). In addition, by progressively changing the size of the probe polymer to smaller size, they were able to examine the distribution of pore size in wet fiber walls. Scallan (55) showed that WRV was directly related to the fiber saturation point (FSP). WRV is the most popular method because of its ease, simplicity and rapidity. WRV and the tensile strength of recycled fibers have been shown to be linearly related (10).

Mechanism of hornification

Reorganization in the cell wall

During drying, due to high and uniform surface tension forces, the microfibrils are re-organized in a better alignment of carbohydrate chains resulting in an intensively bonded fiber structure (19,56,57,59). This phenomenon was named “crack healing” (59). During drying of the fiber, if parts of the adjacent surfaces of cellulose and hemicelluloses coming together match sufficiently well in composition and orientation they could form crystallite zones and consequently restrict swelling on rewetting (60). High drying forces lead to some sort of plastic flow at the crack interface, resulting in strain hardening of the fibers (59). However, in contrast, Bouchard and Douek (25), and Matsuda et al. (61) observed that the recycling of fibers does not increase cellulose crystallinity.

Wetting and drying of the cell wall

Cell wall of fiber swells on imbibing water and shrinks on drying. There are three possibilities for the accommodation of water within the cell wall as postulated by Stone and Scallan (62). Firstly, it could enter capillaries already present in the dry fiber. Secondly, it could form capillaries or pores by separating surfaces that were previously joined. Thirdly, it could form a molecular association with the cell wall components, without creating any new surfaces. About 80% of the water in the cell wall was observed to be in a form of molecular association with the cellulose.

Stone and Scallan showed that the volume of the pores present in the dry cell wall is likely to be small, probably appreciably less than 0.02 cm^3/g, and should have little influence on the relationship between water uptake and the resulting change in cell wall dimensions. Real surface is produced when water is added to dry native cellulose fibers. The diagram of the cell wall in the proposed model is shown in Fig. 2.3 (63). The diagram shows the wall after complete removal of hemicellulose and lignin and therefore composed entirely of the fibrils of cellulose. It is supposed that, in the dry cell wall the fibrils are all tightly packed and totally hydrogen bonded as depicted in Fig. 2.3-A. With the progressive swelling of the structure, bonds between the fibrils are broken leading to the pattern of internal fibrillation illustrated by Fig. 2.3-B to Fig. 2.3-D. Completely swollen fiber consists of several hundred spaced lamellae. The pores developed between the lamellae must fill with water as they are created. Drying closes the pores, leaving the dry cell wall as a continuum containing very few, if any, pores. With complete drying, the structure of the cell wall may be visualized as moving from Fig. 2.3-C to Fig. 2.3-A and then upon rewetting returning to Fig. 2.3-B. The incomplete return is

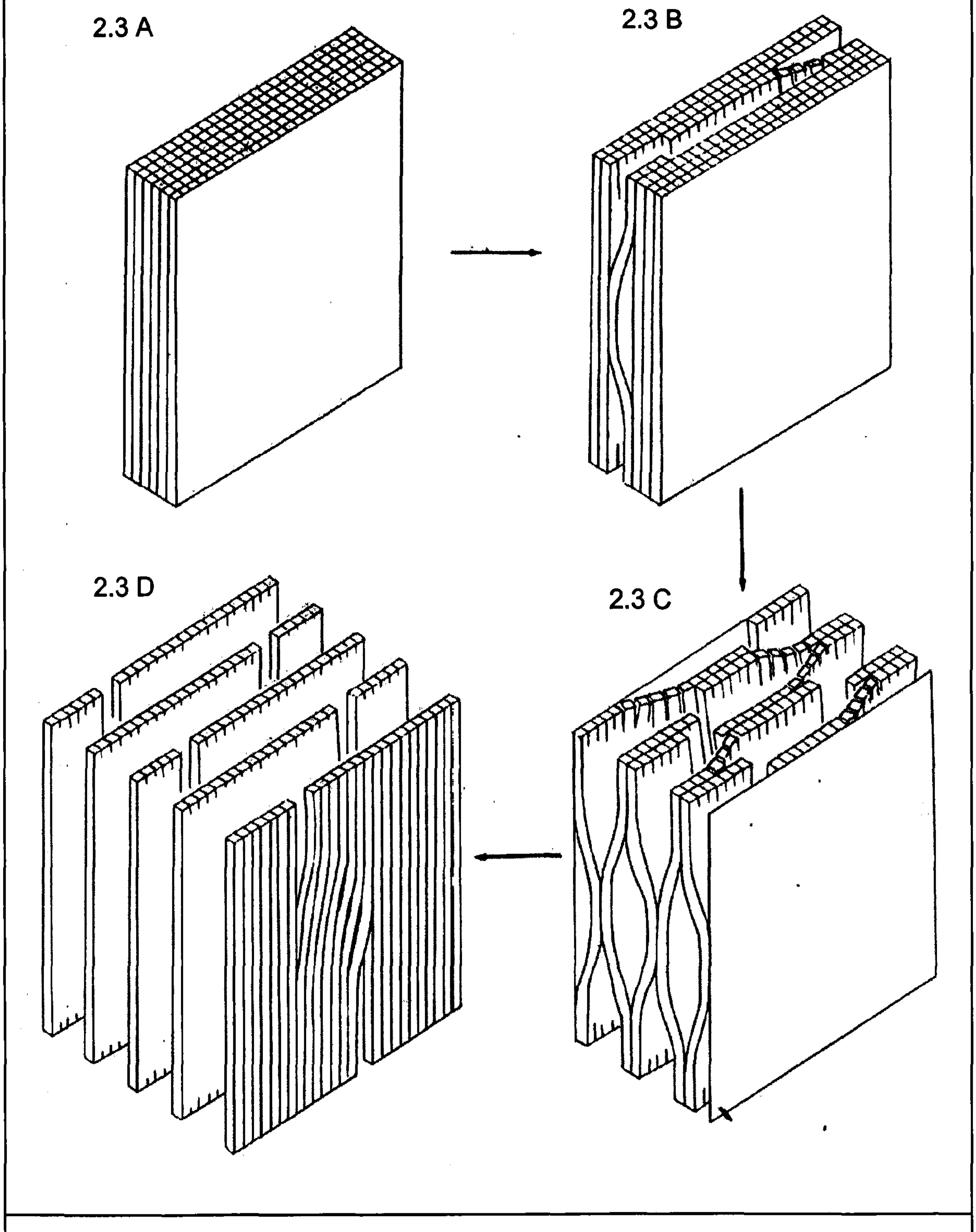

Fig. 2.3: The pattern of internal fibrillation of the cell wall with progressive swelling, as might be expected from the preferential cleavage of tangentially oriented bonds. (Ref. 63)

considered due to hydrogen bonds formed on drying and broken upon rewetting. The final structure (2.3-B) is less swollen and the pores smaller than that of the never-dried fiber. Of course, it is not necessary to go to complete dryness before observing hornification upon rewetting.

Partial drying causes partial hornification. Stone and Scallan (62) argued that there were two types of pore in the cell wall. Pores of one type, approximately half the total volume of the pores (0.08 cm^3/g), close irreversibly during drying. The closure of the pores commences at about 50% moisture and more or less completes at 30-40% moisture. The other type pores start to close in the 30-40% moisture region and continue to close right down to complete dryness, but all these pores can be reopened by a simple swelling treatment with water. Pores that close irreversibly must be located towards the outside of the cell wall and those which close reversibly must be located towards the inside of the cell wall adjacent to the lumen. Refining a dried pulp is shown to aid in reopening the pores that close during drying, but is only successful when the conditions of drying have been mild.

The model may also be used to explain why mechanical and high yield pulps do not exhibit hornification. In wood and high-yield pulps, the wall is represented by Fig. 2.3C with the interfibrillar spaces filled, not just with water, but with ligno-hemicellulose gel (54,64). This ligno-hemicullulose gel prevents formation of irreversible hydrogen bonding between microfibrils during drying. This keeps the spaces between lamellae accessible for water on rewetting (54,65). The chemical pulping process removes the maximum amount of lingo-hemicellulose gel creating free spaces between microfibrils for irreversible H-bonds to form during drying (45). Thus, among the components of cell wall, cellulose is the most involved component in hornification. The recycling potential of a pulp depends upon the amount of lignin

– hemicellulose material that has been removed during pulping and bleaching processes.

H-bonding in the cell wall

Back (66,67) suggested that inter or intra cross-linking of fibers due to higher drying temperatures could be a reason of hornification. He also noted that aging of the paper promotes hemiacetal type crosslinking between cellulose and hemicellulose chains. It may make fiber brittle and restrict them to swell. In contrast, Laivins and Scallan (68) interpreted that such reactions do not occur at room temperature while hornification does.

Lindstrom and Carlsson (69) pointed out that the decrease in WRV could be due to formation of ester between the carboxyl and hydroxyl groups of cellulose during drying. But, Scallan and Tigerstrom (45) observed that the acidic group contents of kraft pulps remain unchanged by drying-and-rewetting and no ester formation between carboxyl and hydroxyl groups could take place during drying.

Hydrogen bonding between hydroxyl groups of adjacent cellulose molecules within the cell wall is considered the primary mechanism responsible for loss of fiber swelling and flexibility in drying-and-rewetting of pulp (61-74). Matsuda et al. (61) showed that the formation of hydrogen bonds take place in the non–crystalline regions of cellulose and hemicellulose but without any additional crystallization.

Milichovsky (75) has suggested two or three types of qualitatively different H-bonds. He proposed that these different types of H-bonds are responsible for oriented (crystalline), less oriented and unoriented (amorphous) zones in the native cellulose. The water causes cellulose to swell rather than dissolve it, presumably, because of the resistance offered by strong H-bonds in crystalline zones. The three types of H-bonds proposed by Milichovsky are:

1. Bonds of irreversible nature:

- Bonds between glycosidic oxygen and hydrogen atoms of several hydroxyl groups such as: C'(6)OH-O(linking)
- Bonds between hemiacetal oxygen and hydrogen atoms of several hydroxyl groups such as C'(3)OH-O(ring), C'(2)OH-O(ring) and C'(6)OH-O(ring).

2. Bonds of reversible nature are the H-bonds between amphoterric primary and secondary hydroxyl groups such as C'(2)OH-C(3)OH and C'(6)OH-C(6)OH.
3. Slightly irreversible type: between primary and secondary hydroxyl groups such as C'(6)OH-C(2)OH.

Therefore the ability to destroy hydrogen bonds with water will depend not only on their strength but also on the nature of the hydrogen bonds (75).

The existence of hydrogen bonding within the cell wall has been experimentally confirmed (68-74). A pulp treated prior to drying by chemicals that prevent formation of H-bonds shows a reduced loss in swelling on drying-rewetting. Ehrnrooth et al. (76) used esterification for the treatment of the pulp fibers. The esterfication of the cellulosic surfaces of the voids in the fiber yields a hydrophobic lining that effectively hinder any permanent healing of the cracks during drying. To support the mechanism of hydrogen bonding and to prevent hornification has been checked by carboxymethylation and methylation reactions (68,69). If sufficient of the hydroxyl groups in a never-dried pulp are replaced by carboxylic acid groups or methoxy groups, the process of hornification can be prevented.

Matsuda et al. (61) also showed that carboxyl groups play a significant role in hornification. Fig. 2.4 shows comparison of WRV of pulp whose carboxyl groups were converted to methyl esters with diazomethane, with those of the original pulp. Value of WRV of methyled fibers is less than the untreated fibers due to the replacement of hydrophilic carboxyl groups to hydrophobic methyl ester groups. However, for handsheets dried at 20°C, WRV for untreated pulp was lower than that of methylated pulp. The difference in WRVs implies that not only hydroxyl groups but also carboxyl groups (in –COOH form) play a significant role in the formation of irreversible intra and/or inter molecular hydrogen bonds in cellulose and hemicellulose under papermaking and drying conditions even at 20°C.

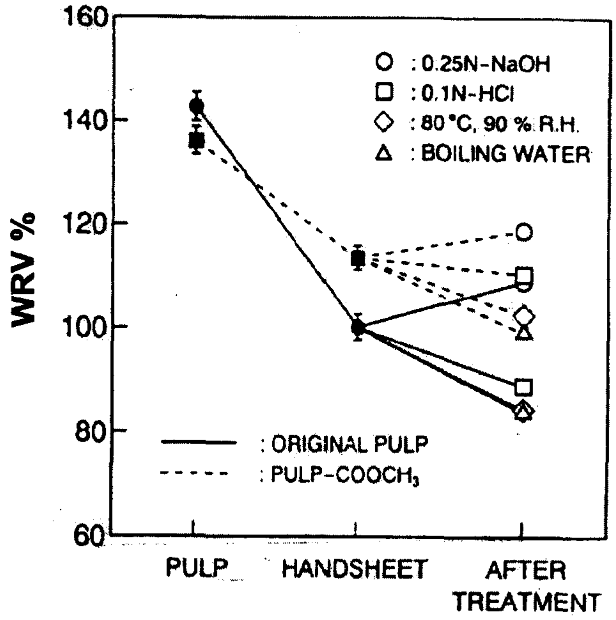

Fig. 2.4: Changes in the WRVs of handsheets prepared from the original pulp and the methylated pulp. (Ref.61)

2.3 FACTORS AFFECTING RECYCLING POTENTIAL OF PULPS

2.3.1 NUMBER OF CYCLES

Several authors have studied the loss in strength of sheet made of recycled fibers as a function of number of recycles (7,8,11-16,18,20-26). The general observation has been that the effects of drying-rewetting are most pronounced in the first cycle and decrease with each successive cycle. Similarly, the reduction in WRV, or FSP is greatest after the first cycle (11,16,20,21,24,27,28).

2.3.2 PULP YIELD

The general acceptance is that fiber swelling on drying of pulps decreases for chemical pulps and remains unchanged for mechanical pulps. Scallan & Tigerstrom (45) have suggested that hornification is a feature of low yield pulps. They studied the swelling ability for series of kraft pulps with yield ranging from 40% to 100%. As the pulp yield decreased loss in swellability of fibers after drying increased. Similar results were also observed for the pulps prepared by acid sulphite pulping indicating that hornification is not specific to a particular pulping process. Klungness & Caulfield (17) also observed that the degree of internal bond formation (hornification) decreased as the pulp yield increased. Mechanical pulps recycle much more reversibly than low yield pulps (11,12,20,21,27,28).

For chemimechanical pulps of aspen in the yield range of 77% to 85%, Law et al. (27) found that WRV and tensile strength decreased with recycling. Apparently the hornification begins when the pulp yield is reduced below 80% - 90% depending upon the wood species.

Scallan&Tigerstrom (45) attributed the irreversible loss of strength for low-yield chemical pulps to its low lignin content. The removal of lignin from the fiber allows greater contact and bonding of carbohydrate components within a fiber. However, the later findings suggest that hemicellulose content plays a greater role in guiding the recycling behaviour of pulps than the lignin removal, Fig. 2.5 (7,17). Cao et al. (7) explained that during drying of high xylan content pulps the xylan molcules between the cellulose microfibrils hold them against the tendency to self-associate. Consequently the cellulose microfibrils remain relatively loose and upon rewetting these fibers regains their flexibility. On the other hand, water occupies voids left by xylans in low xylan content pulps, allowing strong lateral association between the microfibrils and formation of numerous hydrogen bonds during drying. Different from xylan, glucomanan has a stronger affinity with cellulose microfibrils and may even form a crystallized zone with cellulose.

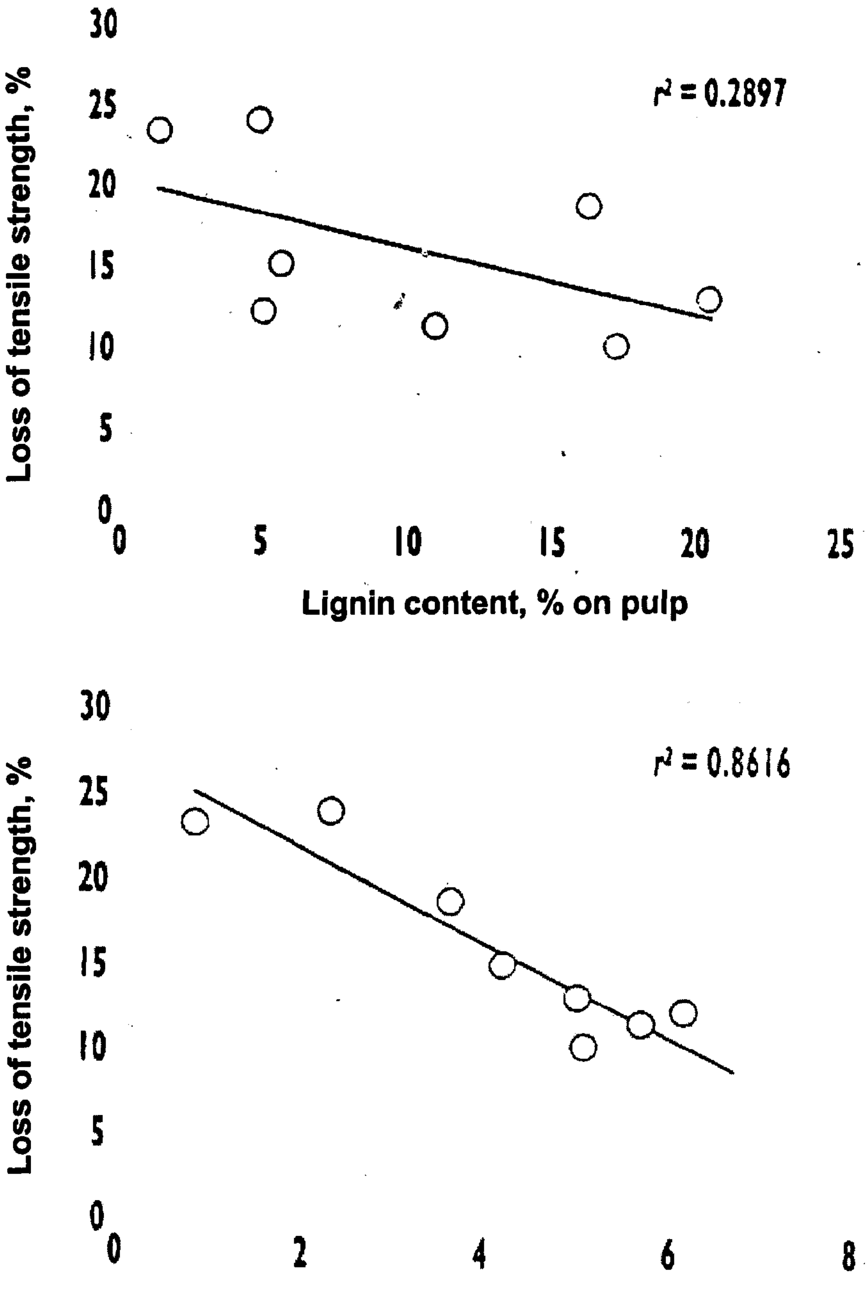

Fig. 2.5: The percentage loss in tensile strength after four recycles as a function of pulp lignin and xylan content. (Ref. 7)

Lundberg and de Ruvo (77) found that the effect of recycling was less pronounced when lignin was selectively removed by chlorination than the continued delignification with alkali where hemicelluloses were also degraded.

For mechanical pulps the observed increase in bonding is because of fiber flattening and increase in fiber flexibility during successive sheet making, pressing and drying cycles. The fiber fattening is defined as simple mechanical deformation with no trans-lumen bonding (20,26). Mechanical pulps are greatly heterogeneous in physical distribution of the fibrous elements. The heterogeneity increases with the specific refining energy input. This heterogeneity plays an important role in determining the recycling characteristic of the pulps as different fiber fractions behave dissimilarly during recycling (28).

2.3.3 REFINING

The greater the degree of refining of the virgin fibers, the greater is the loss in fiber bonding and the related sheet properties on recycling (11,61). High refining of virgin pulp reduces average fiber length and increase fines in the pulp. Recycled fines are supposed to be less effective for improving bonding between fibers. So, the highly refined pulps show low recycling potential.

Another major action of refining is to internally delaminate the fiber and increase it's swelling. These laminations are closed during drying; the large pores created during refining close permanently (62) and prevent fiber from swelling on subsequent wetting.

2.3.4 WATER REMOVAL DURING PAPER MAKING

Drying is the dominating factor in causing hornification of the fiber (10,45,56,57,59,68). Robertson (78) dried a pulp to progressively higher solids content at room temperature and then measured the swelling of the pulp after reslushing. He observed that the reslushed pulp was less swollen the lower the moisture content in the prior drying. de Ruvo and Htun (79) observed the similar results when they used WRV as a measure of swelling. They emphasised that hornification only occurred when the fibers were dried below certain 'critical' moisture content. This critical moisture content was found to be higher for higher initial levels of swelling of the virgin material (Fig. 2.6). Laivins and Scallan (68) noted that the fiber saturation point of undried pulp is numerically equal to the critical moisture content of de Ruvo and Htun.

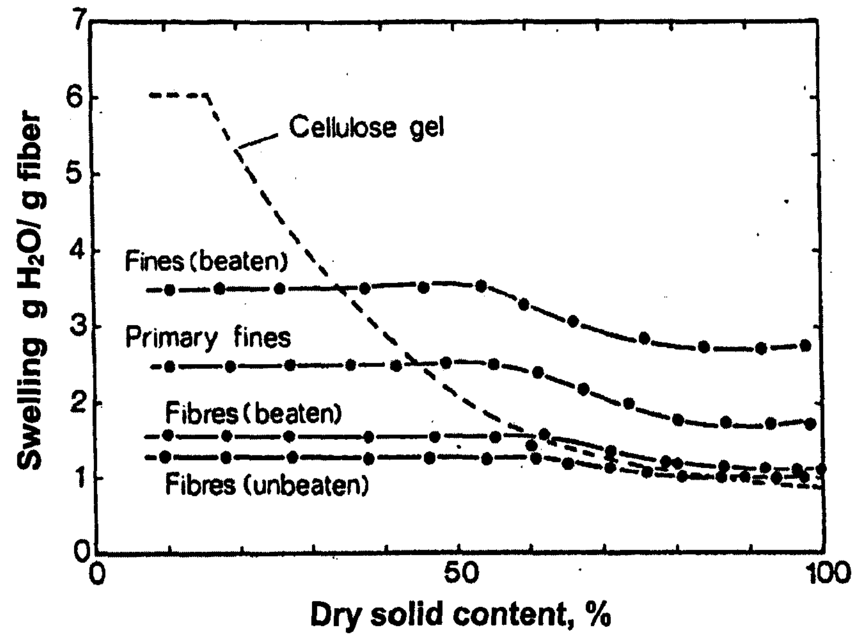

Fig. 2.6: The effects of drying on reswellability of fines and fibers from bleached kraft pulp and cellulose cells. (Ref.79)

It is generally agreed that merely removing water from fiber walls is sufficient treatment to cause the loss of swellability of pulps (68,78-84). The water need not even be removed by evaporative drying: Carlsson and Lindstrom (81) have shown by WRV measurements that hornification can result when water is removed from pulp pads by wet pressing if the moisture content can be reduced below the critical moisture. Maloney et al. (83) measured the effect of wet pressing on fiber and web pore structure using NMR, solute exclusion, and centrifugation techniques. They observed a straight-line relationship between the average pore diameter and the moisture ratio after pressing, implying a preferential dewatering of larger intrafiber pores on pressing. Both reversible and irreversible pore closures were observed.

Many authors have challenged the view that the loss of bonding ability of recycled fibers is entirely due to loss of fiber swelling. Pycraft and Howarth (15) studied the effect of recycling on paper making potential of fibers by using a technique of enzyme degradation of cellulosic fibers. The enzyme reaction was found linearly related with tensile strength of sheet. They found that the enzyme reaction was greater for virgin fiber than for fiber that has undergone drying. The enzyme reaction decreased considerably for drying the fibers in contact with a hot surface. The higher the surface temperature, the greater was the loss in enzyme reaction and hence in bonding potential of fibers. It seems severe drying renders part of the fiber surface inert, and reduces its bonding ability. Wet pressing alone does not adversely affect the surface of fibers provided they are rewetted immediately after pressing. It is drying of the fibers that causes the change, that however depends on the degree of wet pressing (15).

2.3.5 DRYING TEMPERATURE

Pulps dried at higher temperature undergo greater hornification (10,62,79). However the effect of temperature is small in magnitude (62,79). de Ruvo and Htun (62) have shown the values of WRV for pulps dried at different temperatures as shown in Fig. 2.7. Apparently all the swelling gained in the beating of the fibers is lost as a result of drying, even when drying takes place at a low temperature. Higher drying temperatures further reduce the degree of swelling, but this effect is much smaller than that of drying as such. Restraint drying results in more hornification than free drying.

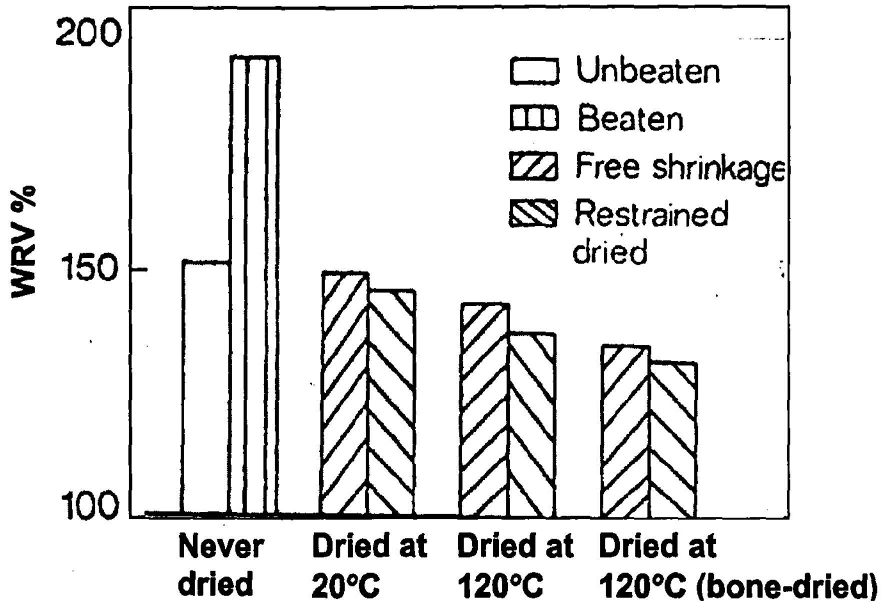

Fig. 2.7: The effect of drying on the WRV. (Ref.79)

Stone and Scallan (62) dried a low yield pulp to zero moisture content at several temperatures prior to reslushing and forming handsheets. Drying – and – reslushing at 25°C dropped the breaking length from 7.3 km for the virgin sheet down to 2.7 km. Raising the drying temperature to 105°C and to150°C further lowered the breaking length to 1.6km and 0.6 km. This indicates that the major reduction in sheet strength is due to water removal, but drying at elevated temperatures causes sever reduction in sheet strength.

2.3.6 WET-END CHEMICALS

Sizing chemicals added to paper are reported to reduce strength properties of the pulp in virgin cycle as well as in subsequent cycles (14,85). The recycling potential of sized papers is lower than that of unsized papers. The rosin-alum sizing causes a greater strength loss than alkyl ketene dimer (AKD) sizing in the virgin cycle, but the recycling potential of AKD sized papers was found considerably worse than that for rosin-alum sized papers (85). Guest and Voss (85) suggested that the sized fibers retain their hydrophobic surfaces and inhibit bonding in the recycled sheet. The retention of hydrophobicity on fiber surface is possibly greater for reactive sizes, such as AKD, than easily water dispersible rosin soap sizes. Forester (86) found that AKD sized paper retained more of its original burst strength, but less of its breaking length.

2.3.7 CALENDERING

Calendering induces irreversible changes in the fiber properties and reduces its recycling potential significantly. Gottsching and Sturmer (36) found that the normal forces in the calendaring nip act destructively upon the fiber structure, and diminish their swellability. This results in reduction in the strength properties such as tensile and tear. The effect of Machine calendering (steel-steel nip) is more severe than calendering in a soft nip. They also found that lightly beaten pulps are subject to more irreversible changes than are heavily beaten pulps.

Calendering flattens fibers leading to a permanent decrease in the bulk of sheets made from recycling of these fibers. Calendering reduces fiber length (14,23); the higher the load during calendaring the more is the effect (14,23). Horn (14), in his recycling experiments, calendered handsheets after drying at each cycle and observed a high reduction in fiber length as well as in strength properties.

2.3.8 POST-MANUFACTURING TREATMENTS

Paper is subjected to cyclic changes in temperature and moisture during converting operations such as surface sizing, coating, and printing. These changes are found to affect the swelling ability of the fibers in their subsequent recycling. Matsuda et al. (61), in a study, measured WRV for handsheets subjected to various treatments, such as, heating at different temperature relative humidity of surrounding air, immersion in boiling water, and soaking in acid or alkaline solutions. Heating of the handsheets in an oven at 100°C or 120°C, decreases the WRV remarkably, irrespective of the freeness of the original pulps. The moisture present in the heating atmosphere influenced greatly the swelling properties of fibers; the greater the moisture the more was the decrease in WRV. Heating for 1hr in boiling water caused a greater reduction in WRV than heating in oven at 100°C. This suggests that heating of fibers in wet conditions results in more hornification than heating in dry conditions. Treatment of handsheets with acidic solution caused a decrease in WRV, whereas, a treatment with alkaline solution caused an increase in WRV.

Fiber swelling is influenced by the temperature of the recycled pulp at the dispersion stage. Swelling of fiber decrease with increasing temperature of the pulp suspension, particularly for temperature above 95°C (33).

2.4 UPGRADATION OF RECYCLED PULP

2.4.1 REFINING OF RECYCLED PULP

Refining of recycled fiber as a means of improving recycling potential has been studied extensively. Some of the findings are as follows:

1. Refining can restore some of the fiber flexibility and swellability of recycled pulp and therefore can enhance the tensile and burst strengths (11,12,87). However, refining also causes severe fragmentation of the brittle hornified recycled fibers. (50,87,88).
2. Refining affects fines and long fiber fractions differently. It is capable of restoring the swelling of long fiber fraction more than the swelling of fines, as fines are permanently hornified. Recycled fines act more as fillers reducing drainage rate of the pulp with little contribution to strength (87,89).
3. The fines generated during refining of recycled pulp show a fast reduction in freeness and slow down the pulp drainage and reduce the production rate on the paper machine (12,87,88). These fines contribute more to the specific surface area of the pulp than its swelling potential. Szwarcsztajn and Przybysz

(89) observed a 70% increase in fine content, when the pulp was refined between two recycles to achieve maximum tensile strength.

4. Laivins and Scallan (37), using solute exclusion technique, examined the effect of refining on swelling behaviour of primary fines (present in virgin refined pulp) and secondary fines (generated during refining of recycled pulp). Some of their results are not in agreement with the earlier findings. They argued that WRV was not as good a measure of swelling potential of fines as the solute exclusion technique, and the contradictions in results appeared because the earlier studies were based on WRV measurements. They observed that PFI mill beating of recycled chemical pulps raised the swelling of fiber and fines to their never dried level, with only small increase in fines percentage. Thus, refining could be used to reverse the hornification of the fiber and the fines. The secondary fines appear to be very different from primary fines in terms of swelling and shape, characteristics that appear to cause them to contribute importantly to the reduction of freeness occurring during refining. Waterhouse and Omori (89) inferred from drainage measurements that the secondary fines had a greater hydrodynamic surface area and were, therefore, more effective than primary fines in enhancing sheet densification and properties.
5. One study (91), on primary and secondary fines of TMP, Karft, and recycled paper, revealed that the recycled pulp fines (both primary and secondary) are almost as effective as the virgin kraft fines in improving handsheet strength properties. Primary fines are slightly better in improving density and tear, while secondary fines are better for tensile, burst and fold of recycled pulp stock.
6. Recycled fibers have the cross-sectional shapes generally collapsed. The extent of collapse is less for fibers of thicker wall. On refining of these fibers, wall

thickness increases as it steadily swells towards lumen, but the outer diameter decreases as surface parts of the fiber are removed (33, 92).

7. Low consistency refining at low specific edge load can be used for improving the bonding ability of recycled fibers (93,94,95) but with the associated increase in fines content and drainage resistance (33).
8. High consistency refining (30%) can be used to save fiber from excessive fragmentation (96,97,98). High consistency refining produces pulps of higher tear strength but slightly lower tensile and burst strength. This may be due to increased curl and microcompressions to the fiber that in turn reduce its uniform stress distribution characteristics on loading (44). Chemical fiber suffers such deformities more than mechanical fiber. However, high consistency refining consumes much more energy than low consistency refining. Low consistency refining after a high consistency refining can remove curl in the fiber, which increases tensile strength of the paper made from recycled pulp (99).

2.4.2 ALKALI TREATMENT OF RECYCLED PULPS

In waste paper processing sodium hydroxide is used to enhance fiber separation and ink detachment from the fiber surface by solubilizing the ink binder. Sodium hydroxide up to 1.5% of o.d. fiber is permissible for high yield pulps and 3 to 5% for low yield chemical pulps (100). Alkali also increases the swelling potential of recycled fibers, and hence the strength properties of the paper made from these fibers. Alkali treatment increases freeness, fiber flexibility and surface conformability (101,102).

In an experimental study by Matsuda et al. (61), handsheets were subjected to alkaline and acidic treatments. The acidic treatment resulted in a decrease in WRV, while alkali treatment increased WRV irrespective of the degree of beating of the treated handsheets as shown in Fig. 2.8. Three possible mechanism were suggested for the increase in WRV by alkali treatment:

1. Partial cleavage of hydrogen bonds formed between carboxyl and alcoholic hydroxyl groups in the paper sheet.
2. Partial cleavage of hydrogen bonds formed between alcoholic hydroxyl groups.
3. Conversion of pulp -COOH to more hydrophilic pulp -COO$^-$ form.

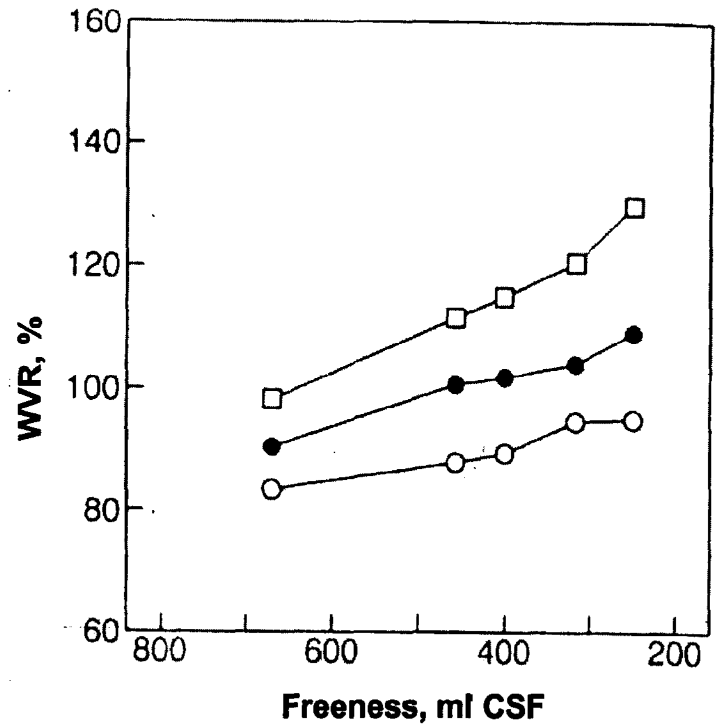

Fig. 2.8: WRVS of handsheets soaked in acid and alkaline solutions as a function of the freeness of the pulps used for handsheet making. Handsheets were: original (●), and soaked in 0.1 mol/L HCL (O) and 0.25 mol\L NaOH (□). (Ref.61)

Mechanism of Fiber Swelling by Alkali Treatment

Donnan equilibrium

The degree of fiber swelling is affected by the acidic groups present in the pulp (103,104,105). Some of these groups are originally present in wood and others are introduced through pulping and bleaching processes. Most of the acidic groups originate from the noncellulosic residues in the fiber wall. The cell wall may be considered a macromolecular gel to which these acidic groups are bound (105). In the presence of water, a fraction of these groups dissociates, releasing mobile counter-ions into the gel. A concentration of ions within the gel that is greater than in the external aqueous phase is therefore created. Osmotic pressure draws additional water into the cell wall, and swelling continues until the reduced osmotic pressure differential is balanced by the residual cohesive forces of the wall. As the ions must remain in vicinity of the acidic groups to remain electrically neutral the only way the difference in osmotic pressure between the interior and exterior of the wall may be overcome is by drawing additional water into the cell wall. Thus by increasing the acidic group content of a pulp swelling may be enhanced (103-105).

While the presence of acidic groups is a basic requirement for the type of swelling mechanism proposed, the nature of counter-ions of the groups is also of great importance. It is the number of counter-ions that are released into the solution that controls the osmotic pressure. In most pulps, the acidic groups are of the weak carboxylic type. Therefore if the acidic groups are in hydrogen form they will only be dissociated to a small degree. On the other hand if the groups are in the form of sodium salts, the dissociation will be largely complete, and swelling will be at a maximum for the number of acidic groups. Where the carboxylic groups are in the form of salts of multivalent cations, the number of ions released into the solution will be intermediate between the hydrogen and sodium cases. Primarily there will be an effect of valency. First, for a given number of acidic groups, the ions will be proportionally fewer the higher the valency. Second, there is a tendency for the degree of dissociation to be lower when the valency is higher.

If the mixture of counter-ions normally present in pulp is removed and replaced by single species, it is found that the paper made from the pulp is increasingly stronger in the order of (105):

$$Fe^{+++} < Al^{+++} < H^{+} < Ca^{++} < Mg^{++} < NH_4^{+} < Na^{+}$$

In mill conditions commonly present cations is calcium ion. Alkali treatment during processing would replace some of these counter-ions of the acidic groups by sodium and contribute to fiber swelling to some extent (106). If the presence of metal ion increases in the process, the effect of alkali on fiber swelling is reduced (33).

Mechanical pulps are low in acidic groups content and low in swelling. Several of the chemical methods used to upgrade the strength of mechanical pulp involve large increases in the acidic group content and hence the fiber swelling. Acidic group content of mechanical pulps can be increased by treating them with caustic soda and ozone (104). Extra acidic groups are generated as a result of the hydrolysis of easters and lactoses in the hemicelluloses of mechanical pulps (29,104). Upgrading of mechanical pulp by sulfonation of the chips prior to refining may also be due to increase in acidic group content.

In chemical pulping, initially the acidic group content rises rapidly as a result of the hydrolysis of the esters in the wood and degradation of carbohydrates. A maximum acidic group content of over 300 meq/kg is achieved before the material bearing the acidic groups dissolves from the fibers. For pulps with high cellulose content (low yield) acidic groups are not important for the swelling (64).

Alkali treatment of unbleached kraft in sodium form after drying and rewetting found high increase in FSP than to hydrogen form. Bleached Kraft pulp of both sodium and hydrogen forms on treatment with sodium hydroxide after drying and wetting found no significant effect on the swelling level (64,106). The presence of sodium hydroxide during recycling has only small effect on the swelling level of the kraft pulps. It is likely that hydrolysis of the ester groups had already occurred during kraft pulping. Thus subsequent treatment with sodium hydroxide does not produce acidic groups and there is no change in the level of swelling (106).

The most widely used method of increasing the swelling of low yield pulps is carboxymethylation – a method which augments the acidic group content by substitution of carboxylic groups (-COOH) for hydroxyl groups (-OH). Graft polymerization of acrylonitrile onto chemical pulps is another method of increasing swelling. The high swelling is only observed after the graft polymer has been partially hydrolysed to polyacrylic acid (105).

Studies have been undertaken to compare the quantitative effect of refining and alkali treatment on recycled pulps (107). Refining provided greater recovery, than the separate alkali and HSF treatments. But, a combined alkali/HSF treatment provided better recovery than refining and in some cases was comparable to virgin pulp for both, unbleached and bleached kraft.

The effect of beating in a PFI mill of alkali treated OCC furnish shows high freeness than the untreated pulp, due to relaxation of individual fibers (102). Fig. 2.9 shows that the sodium hydroxide treated sample have greater strength then the untreated (control) at the same freeness.

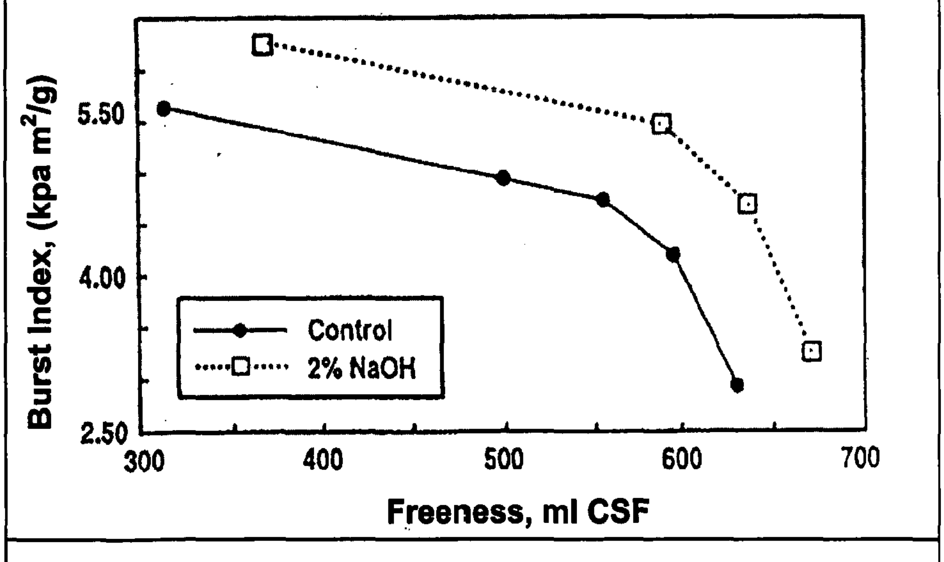

Fig. 2.9: Effect of refining on burst index. (Ref. 102)

2.4.3 FRACTIONATION OF RECYLED PULPS

The quality of recycled pulp can be enhanced by fractionating it into a long fiber fraction and a short fiber fraction, and processing the two fractions separately. The following strategies have been suggested (108-109):

1. Utilization of the two fractions in the productions of two different paper grades on two paper machines.
2. Utilization of the two fractions in two or more plies of one paper sheet.
3. Remixing of the treated long fiber fraction with the untreated short fiber fraction. Putz et al. (109) have observed only minor advantages in strength characteristics by fractionation and separate activation if both stock components are remixed.

Fractionation is advantageous for energy saving in refining and/or dispersion due to the fact that only a part – the long fiber fraction – of the total stock has to be treated. Beating and/or dispersion of long-fiber fraction improve its characteristics and reduce the flake content. The improvement of the optical properties is especially significant in dispersion but also in beating. Many West German board mills are using fractionation to upgrade low quality wastepaper (109). The dominating field of fractionation is in the production of corrugating medium and liner.

In a laboratory study (110), mixed office waste was collected, pulped, and cleaned. Handsheets were formed, repulped, and reformed to obtain pulps representing four recycles. A portion of the pulp from each cycle was fractionated to obtain long and short fiber fractions using Bauer McNett fiber classifier. It was observed that the recycling process had a greater detrimental effect on the short fiber than on the long fiber. Long-fiber fraction had much better characteristics than the mixed pulp.

2.4.4 USE OF STRENGTH AIDS

Dry strength aids are used to enhance fiber-fiber bonding (111-113). They can be used to substitute for the refining and prevent generation of excessive fines that is critical in recycled pulps. When polyacrylamide based dry strength aids are used the added advantage is that the drainage and drying rate improves without materially affecting the sheet formation (112).

Bhardwaj et al. (113) observed that anionic polyacrylamide at a dose level of 0.04% for secondary fibers containing corrugated Kraft cuttings and corrugated boxes, showed about 40% increase in tensile and burst strength and 52% to 56 % increase in drainage rate. The performances of cationic and amphoteric starches on drainage improvement were similar. The starches improved drainage by about 32% at the dose level of 1.25%. The amphoteric starch showed high gain in tensile index and TEA.

However, the dry strength aids are not a full substitute for refining in restoration of the swelling ability in hornified fibers (33), as the penetration of these additives into micropores in the cell wall structure is limited due their molecular size.

2.4.5 USE OF ENZYMES

Cellulase and hemicellulase are the principal enzymes used for fiber modifications. The major gain by enzyme hydrolysis of recycled pulp is reported to be an increase in freeness (113-116). As far as the effect of enzyme on strength properties of pulp is concerned, opposite views are expressed in the literature. Oltus et al. (117) reported that enzymatic hydrolysis initiates fracturing of fiber, ultimately resulting in complete fiber disintegration. They concluded that no revitalization of the waste paper fiber could be acquired through enzymatic treatment and a decrease in tensile, burst and tear strength was observed.

In contrast to the findings of Oltus et al., Pommier et al. (114) showed that the strength did enhance by enzyme treatment of secondary fibers. Mechanical refining preceding enzyme treatment can give better physical properties at same freeness level. It was suggested that the enzymes act preferentially on fibrils present at the fiber surface since they have extremely high specific area. A controlled enzyme reaction will remove only very small components of the fiber surface and fines that have great affinity for water, but do not contribute to the hydrogen bonding. Thus, the pulp drains more easily, without suffering a loss in mechanical properties.

Bhut et al. (107) agreed with Pommier et al. (114); freeness increase due to enzyme treatment was greater for bleached softwood pulp than unbleached pulp because of greater accessibility of cellulose for enzymes in bleached pulp. The lignin in the unbleached pulp may hinder the attack of enzyme on cellulose.

An important observation is that freeness increases at the beginning of the enzyme hydrolysis, and excess contact time leads to fiber degradation and loss of yield (114,115).

Jackson et al. (115) proposed that in addition to hydrolyzing fines and fibrils on fiber surface, enzyme could flocculate fines and small fiber particles resulting in increase in freeness. Stork et al. (116) added that the improvement of drainage is caused mainly due to enzymatic degradation of fines fraction rather than the surface cleaning of long fibers.

The enzyme process is simple to adopt, the operational conditions are close to the classical conditions found in the recycle paper industries i.e. 3% consistency, 30°C to 50°C temperature and pH range between 4.8 to 6.5 (114). The reaction time of about half an hour is adequate. Appropriate and controlled conditions can increase freeness with no or little loss in mechanical properties. Fiber length is not affected at low enzyme concentrations and short reaction time. The effect of enzyme treatment can increase 40% in drainage properties without any substantial change in strength property.

CHAPTER 3

PREPARATION OF PULPS FOR THE STUDY

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PREPARATION OF PULPS FOR THE STUDY

3.1 INTRODUCTION

Wheat straw and bagasse are promising fibrous raw materials for fiber deficient countries like India. Bagasse is residue of sugar cane, after its juice has been extracted by crushing in a sugar mill. Wheat straw is the residue of wheat stalk, usually mixed with leaves and chaff, after the grain has been removed by threshing.

The literature reveals that there are large variations in chemical composition of these raw materials depending on the variety of the crop and the region of cultivation (118-136). For example, the lignin content within wheat straw or bagasse varies between 14% and 24%. These variations will affect yield and properties of the pulp produced from them. The following generalizations, however, can be made.

1. Open structure and low lignin content enable pulping and bleaching of these raw materials easier than woods. Removal of pith from bagasse is essential for producing high quality pulp by chemical or mechanical process.
2. Soda process is commonly used for pulping of these raw materials as the sulphate process has little advantage in terms of yield and strength properties. Soda pulps of these raw materials may be bleached with fewer bleaching steps and lower chlorine demand than sulphate pulps.
3. For delignification, wheat straw offers greater resistance to chemical penetration, consumes more chemicals, and needs longer cooking time than bagasse. Wheat straw pulp has slower drainage characteristics than bagasse pulp.

3.2 SELECTION AND PREPROCESSING OF RAW MATERIALS

Pulps used for the recycling study were prepared in laboratory from wheat straw and bagasse. Wheat straw was procured from a nearby village area in the month of May (harvesting time) after the wheat was separated from the straw in a thrashing operation. The procured straw (about 10% moisture) was screened on a 20-mesh screen in dry condition and then washed with water to remove extraneous dirt. About 15% of the total wheat straw was rejected in the dry screening and washing operations. The rejected material was largely noncellulosic.

Fresh bagasse was procured from a nearby sugar mill in the month of February and was air-dried. The dried bagasse was depithed in a laboratory dry-depither and then washed on a 20-mesh screen to remove the pith and dirt. The mass rejected in depithing and washing was about 30% of the total air-dry bagasse.

3.3 PROXIMATE ANALYSIS OF THE RAW MATERIALS

The proximate analyses of the screened and washed raw materials are given in Table-3.1. Relevant Tappi test methods (137) were used for the analyses.

Table- 3.1: Proximate Analyses of Raw Materials.

Particulars	Bagasse	Wheat straw	Method
Hot water Solubility (%)	2.7	9.3	T207
1% NaOH Solubility (%)	30.2	38.3	T212
Alcohol-Benzene Solubility (%)	1.6	3.4	T204
Holocellulose (extratives free) (%)	76.0	73.5	Laboratory Method
Alpha cellulose (extratives free)(%)	44.4	41.8	Laboratory Method
Lignin (extratives free) (%)	20.7	21.3	T222
Ash (%)	1.2	6.6	T211/T413

* These values are averages of analyses of three samples.

3.4 BLEACHED CHEMICAL PULPS

The screened raw materials were cooked by soda process in a laboratory batch digester. The pulping conditions used are given in Table- 3.2. The pulps were washed, screened, and bleached using CEHH sequence. Presently CEHH or CEH are the sequences most widely used by the Indian industry for bleaching of agro-residue pulps. The conditions used in bleaching are given in Table- 3.3 and Table- 3.4.

3.5 SEMI-CHEMICAL PULPS

The screened and washed raw materials were used to prepare semi-chemical pulps of wheat straw and bagasse. Procedure of pulping is as given below.

1. 500g (o.d. basis) raw material was soaked for 15 minutes in a dilute caustic soda solution to have an even penetration of alkali in the raw material.
2. The soaked raw material was drained over a synthetic cloth and squeezed to a level that only required amount of alkali (on o.d. raw material) remained absorbed in the material (4% for bagasse and 5% for wheat straw) and the excess alkali was drained.
3. The soaked material was then heated to 100°C and maintained at that temperature for 30 minutes in a laboratory autoclave.
4. Immediately after cooking, the material was refined in a Sprout-Waldron single disk refiner. The distance between the refiner disks was kept 100 μm (4-thous) for the first pass through refiner and 75 μm for the subsequent three passes.
5. The consistency was between 20% and 22% for the first pass, between 12% and 15% for the second and third pass, and 8% for the fourth pass.
6. After refining the pulp was disintegrated in a 20L laboratory disintegrator at 3% consistency and 80°C temperature for 20 minutes.

Table 3.2: Pulping Data

Conditions	Wheat straw		Bagasse
Alkali charged (%)	16	16	15
Bath ratio	1:5	1:5	1:5
Cooking Temp. °C	170	160	170
Time to Temp. (min)	75	90	90
Time at Temp. (min)	75	100	30
Total yield (%)	-	49.8	56.7
Screened yield (%)	42	49	56
Kappa Number	18.5	24	22.5

Table 3.3: Conditions of bleaching.

Conditions	C-Stage	E-stage	H-stage
Consistency (%)	3	10	10
Temperature °C	25 (ambient)	60	40
Retention time (min.)	45	60	150
End pH	2-3	9-9.5	9.5-10

Table 3.4: Chemicals charged during bleaching and bleaching results.

	Wheat straw		Bagasse
	42% Yield	49% Yield	56% Yield
Bleaching sequence	CEH	CEHH	CEHH
Kappa factor used	0.25	0.3	0.25
% of total chlorine charged			
In C-Stage	70	65	70
1st H-Stage	30	22	15
2nd H-Stage	-	13	15
Alkali Charge in E-stage (%)	2.0	2.6	2.4
Shrinkage (%)	6.75	10.5	8.5
Brightness (%)	74	81.7	82
1% NaOH solubility	8.96	7.81	5.74
α-Cellulose (%)	77.72	77.30	82.90
β-Cellulose (%)	7.27	10.00	11.20
γ-Cellulose (%)	15.01	12.70	5.90

7. The disintegrated pulp was screened in a laboratory screen having 0.25mm wide slots. Finally, the pulp was filtered on a 250-mesh synthetic cloth.
8. The pulps produced were analyzed using appropriate Tappi test methods.

The proximate chemical analyses of the prepared semichemical pulps of wheat straw and bagasse, and the commercial CMP procured from an Indian mill are given in Table- 3.5.

Table-3.5 Proximate analysis of higher yield pulps.

	Semichemical Pulp		Bagasse CMP
	Wheat straw	Bagasse	
Extractives (%)	0.36	0.19	0.74
Lignin (%)	7.01	6.92	16.12
Holocellulose(%) (Extractive free)	89.83	92.05	82.48
Ash (%)	1.86	0.89	1.73

3.6 CODING OF PULPS

In further discussions, the pulps studied have been referred to by their codes as defined in Table- 3.6.

Table 3.6: Pulps used in the recycling study.

	Pulping	Unbleached Yield	Bleaching	Brightness	Code
Wheat Straw	Soda pulp	42%	CEH	74%	WCP42
Wheat Straw	Soda pulp	49%	CEHH	82%	WCP49
Wheat Straw	Semichemical pulp	60%		48%	WSCP60
Bagasse	Soda pulp	56%	CEHH	82%	BCP56
Bagasse	Semichemical pulp	65%		50%	BSCP65
Bagasse	Chemimechanical pulp (Mill made)	-	Peroxide	50%	BCMP

CHAPTER 4

RECYCLING POTENTIAL OF PULPS

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RECYCLING POTENTIAL OF PULPS

4.1 INTRODUCTION

The basic approach in study of recycling of paper consists of slushing/beating of the virgin pulp, formation of handsheets/pads, pressing, and drying of the sheets. A few of the sheets formed are used for testing and the rest are reslushed for the next cycle. Fig. 4.1 shows a schematic diagram of the laboratory experiments conducted by different researchers. The variations have been in pressure applied during wet pressing, the temperature and restraint to shrinkage during drying, and refining of the virgin and recycled pulps. Some workers (14,23,24,29) have also included operations like calendaring, printing and deinking between the cycles.

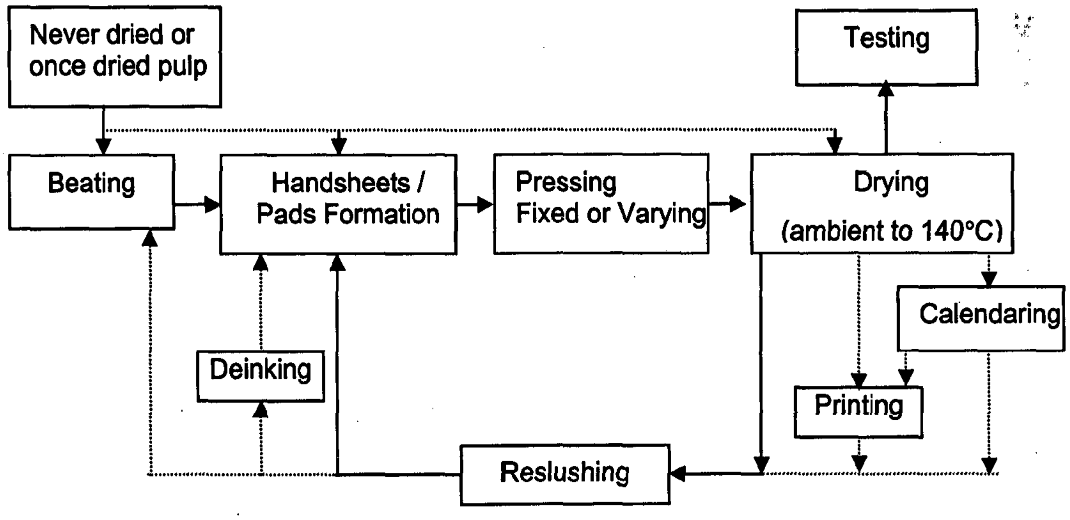

Fig. 4.1: Schematic representation of repeated papermaking process used by various scientists in their recycling studies. The optional processes adopted are shown by dotted lines.

The classic handsheet recycling experiments may not truly represent the industrial papermaking from the secondary fiber. For example, hardly ever is paper made from a furnish consisting entirely of wastepaper of the same grade (138). Szwarcsztajn (139) pointed out that making a handsheet differs from making paper on a machine with respect to the consistency of the stock, formation under static or dynamic conditions, restrained or free drying, and closed or open water circuits. But these variations could cause only quantitative differences in sheet properties rather than qualitative differences. He opined that too much attention to the scale of these differences was unnecessary. The properties such as freeness, specific surface, and water retention value of recycled pulp and its fiber fractions can help to understand the mechanism of deterioration of a pulp during recycling. Eastwood and Clarke (48), from recycling experiments using handsheets and paper made on pilot machine, observed similar trends in change in properties with the progress of recycling for both types of sheets. However, on recycling, the changes in properties of sheets made on pilot machine were smaller than for handsheets.

4.2 EXPERIMENTAL WORK

4.2.1 PULPS USED FOR THE STUDY

Five single specie pulps of varying yields, prepared from wheat straw and bagasse (Chapter-3, page 47-51), and one commercial chemimechanical pulp of bagasse were used for the study. For reference the pulps were coded as given in Table-3.6 (page 51). At the beginning of the recycling experiments the pulps WCP42, WSCP60 and BCP56 were in their never dried state, and the pulps WCP49, BSCP65 and BCMP were in their air-dried state.

4.2.2 EXPERIMENTAL PLAN

The experiments used in the present study are shown schematically in Fig. 4.2. Recycling was limited to drying and rewetting of pulps and the sheets between the cycles were made on a laboratory sheet-making machine. The initial freeness of the pulps used for recycling study was kept in the range of 350 to 300 ml CSF. Chemical pulps were beaten in a valley beater to achieve the desired freeness. Semichemical pulps were obtained by refining to the desired freeness in a laboratory sprout waldron refiner. From a portion of the beaten pulp, handsheets of

60 g/m^2 were prepared according to the standard method SCAN M5: 76 (140) for the evaluation of various properties of the pulp. The handsheets were wet pressed and air-dried as specified in the standard procedure. To speed up the experimental work, thick pads (350 – 450 g/m^2) were prepared on the same sheet-making machine from the remaining portion of the pulp. Making of pads in recycling experiments has been reported by Chatterjee et al. (21). The pads were wet pressed (700 kN/m^2) and dried on a heated cylinder at 80 °C. The handsheets and the pads were dried in contact with gloss plates. The backwater was re-circulated during the making of sheets and pads. For subsequent cycles the pads were reslushed in the laboratory disintegrator at 1.2% consistency and remade into handsheets and pads without beating in between.

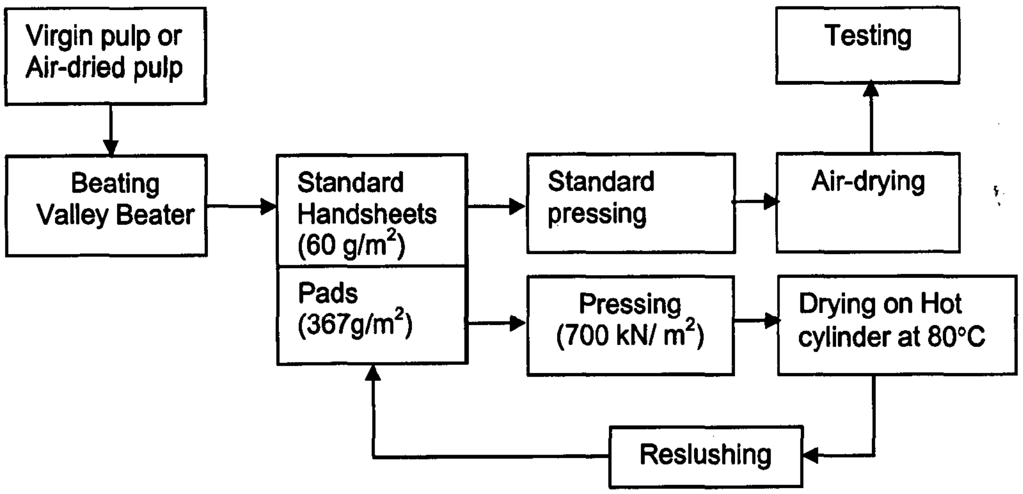

Fig. 4.2: Schematic representation of repeated paper making process.

4.2.3 EVALUATION OF PULP PROPERTIES

Measurement of Water Retention Value (WRV)

WRV is an important parameter to measure the affinity of pulp towards water. It is the amount of water held by the pulp after subjecting it to a specified centrifugal force. Different values of centrifugal force are reported (10,53,55,58,141,142).

Some used 30N force, while some used 9N force. We found from several experiments that a centrifugal force of 30N for 15 to 30 minutes gave a stable and reproducible value of WRV. The experimental details and results obtained are given in Appendix-1.

Pulp Properties

Pulps were evaluated for properties as per relevant Tappi and other standard methods as given in Table- A2.1 (page 134). The fiber classification of the pulps was done at 1, 2, 4 and 6 cycles in a Bauer-McNett classifier. The results are given in Table-4.1 (page 69). The effects of recycling on pulp freeness, WRV and drainage time are given in Table- A2.2 (page 135). The properties evaluated from the standard handsheets at different cycles for six pulps are given in Tables- A2.3 to A2.8 (page 136-140). Chemical bleached pulps are also evaluated for alpha, beta and gamma celluloses at first and fourth cycles to check the loss in these cellulose contents due to recycling, given in Table- 4.2 (page 70).

4.3. RESULT AND DISCUSSION

4.3.1. BAGASSE CHEMICAL BLEACHED PULP

Freeness, WRV, Apparent Density, and Scattering Coefficient

Freeness, WRV, apparent density, and scattering coefficient of pulp have been plotted against number of cycles in Fig. 4.3. The freeness (CSF) of bagasse chemical pulp was found to increase with recycling by about 22% after six cycles. It may be noted that the pulp was defibrated in a laboratory disintegrator without any refining. Earlier workers, who studied the effect of recycling on freeness of wood pulps, found no definite relation between freeness and number of cycles. Some observed an increase (11,16), some observed a decrease (20), while others observed no change (18) in freeness on recycling of pulp. Perhaps, some of the

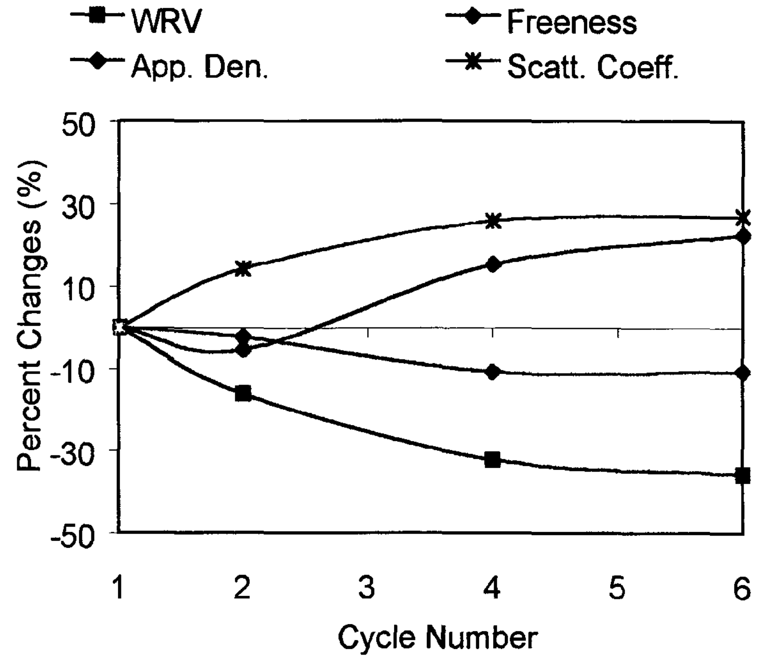

Fig. 4.3: Effect of recycling on physical properties of BCP56 .

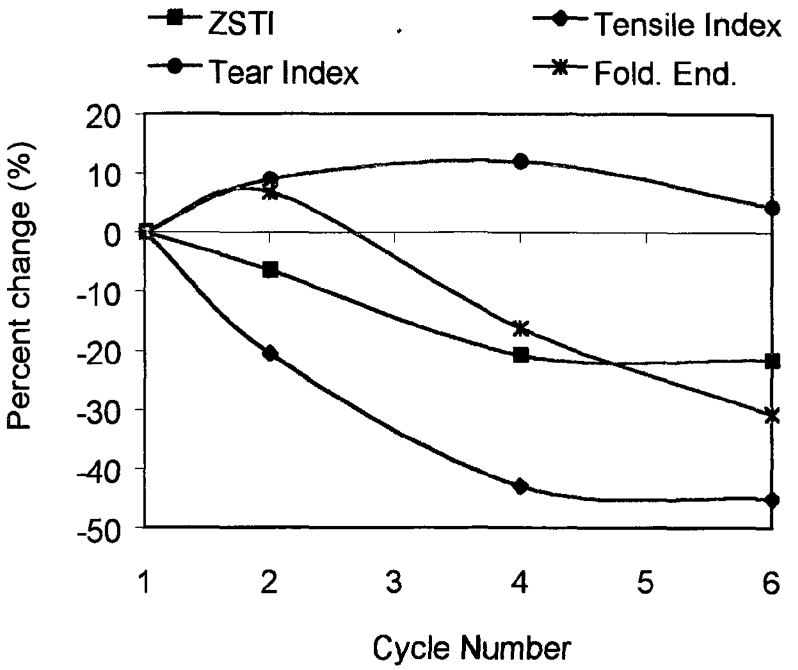

Fig. 4.4: Effect of recycling on strength properties of BCP56.

discrepancy in the above observations is due to large difference in the initial refining of the pulps (500ml to 200ml) (Chapter -2, page 8).

WRV of bagasse chemical pulp decreases by about reduction after six cycles. Apparent density decreases with recycling and scattering coefficient increases. After six cycles, the decrease in density is about 10% and increase in scattering coefficient is 27% of the initial values. Gurley air resistance decreases with recycling. Porosity measured by print-surf method exhibits a rise with recycling. The roughness of handsheets increases on recycling (Table- A2.3, page 136).

Strength Properties

Fig. 4.4 shows the effect of recycling on strength properties of bleached bagasse chemical pulp. The tensile index decreases and the tear index increases with recycling. This behaviour is quite similar to that of softwood and hardwood pulps reported in the literature (11,14,16,20). The zero-span tensile index also decreases on recycling with about 21% after six cycles.

It is reported in the literature that for softwood and hardwood pulps the change in properties is most significant after the first cycle, and less significant in subsequent cycles. In contrast, for the bagasse chemical pulp more or less a gradual decrease in tensile index with recycling is observed. Tensile index decreases by 45% after sixth cycles. Yamagishi and Oye (16) reported 60% and 49% loss in tensile index after six cycles for bleached kraft hardwood and softwood pulps respectively. The freeness level and drying temperature were the same in the experiments of Yamagishi and Oye as are in our experiments. The burst index for bagasse chemical pulps follows a similar trend as the tensile index with a 60% drop after six cycles. Folding endurance also decreases on recycling with about 30% decrease after six cycles.

4.3.2 WHEAT STRAW CHEMICAL BLEACHED PULPS

Freeness, WRV, Apparent Density, and Scattering Coefficient

Fig. 4.5 shows the changes in the physical properties of wheat straw chemical pulps (WCP42 and WCP49) on recycling. The pulps show a decrease in freeness on recycling. The greatest drop occurs after first cycle; it is about 20% for WCP42 and 28% for WCP49. Drop in freeness seems to be related to the fines content in the pulp. WCP49, which has a higher percentage of fines, shows a higher drop in freeness than WCP42 on recycling (Table- 4.1, page 69).

WRV of pulps decrease during recycling. After six cycles percentage reduction in WRV is 33% for WCP42 and 15% for WCP49. Yamagishi and Oye (16) reported about 13% reduction in WRV for softwood and hardwood bleached kraft pulps after six cycles. The WRV for wheat straw chemical pulps decreases gradually with the number of cycles, unlike wood pulps where the major loss in WRV or FSP is reported to occur in the first cycle.

Changes in apparent sheet density on recycling of the wheat straw chemical pulps are relatively very small compared to wood pulps (20). Scattering coefficient of handsheets increases with number of cycles for both the pulps. WCP42 shows about 23% and WCP49 about 4% increase in scattering coefficient after six cycle. It indicates that loss in fiber bonding on recycling is more for WCP42 than for WCP49.

Gurley air resistance of the sheets of wheat straw pulps decreases on recycling. For WCP42 the Gurley value drops by 89% after the first cycle and remains nearly same on subsequent recycling. For WCP49 the drop in Gurley value is less about 28% in six cycles. Print-surf roughness increases on recycling of wheat straw chemical pulps. WCP42 shows higher increase in paper roughness than WCP49 (Tables- A2.4 & A2.5, page 137,138).

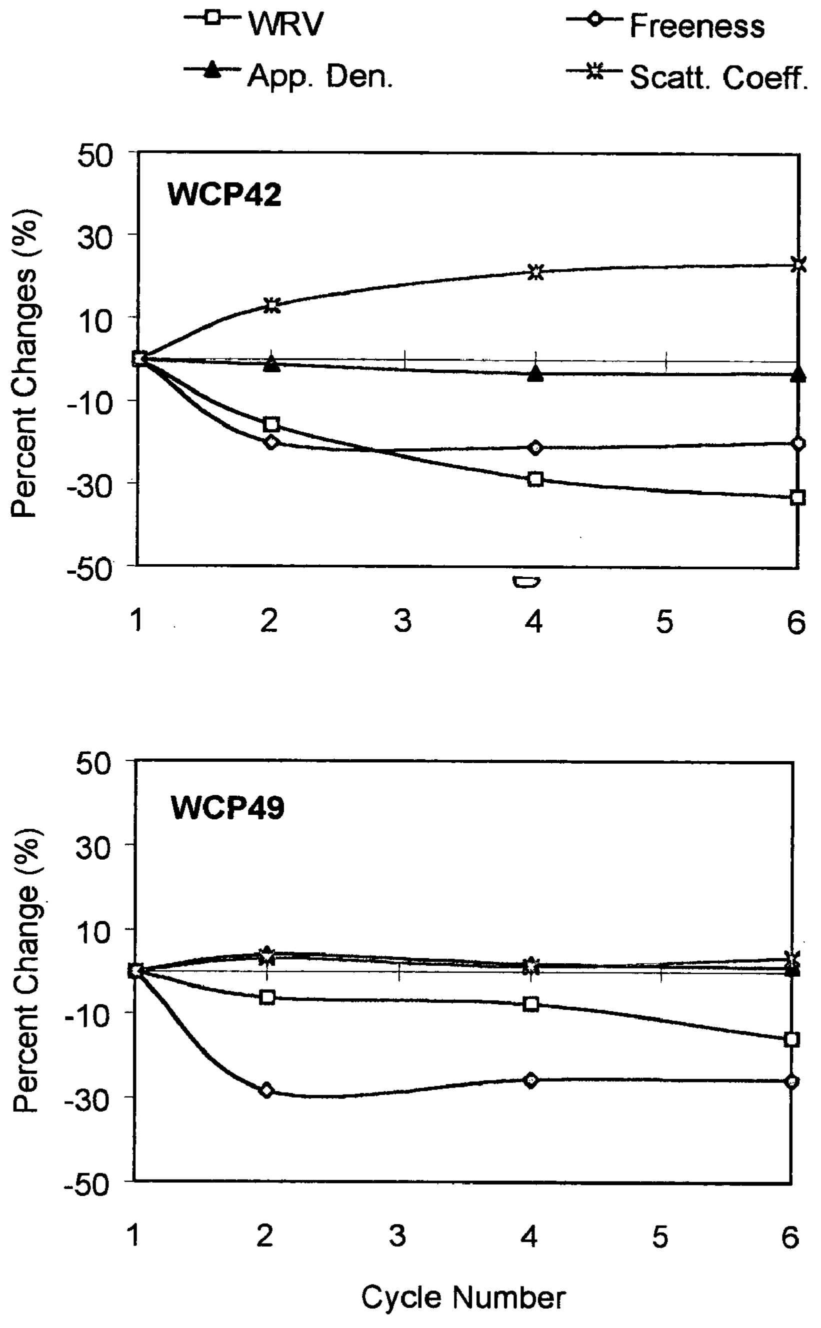

Fig. 4.5: Effect of recycling on physical properties of WCP42 and WCP49 .

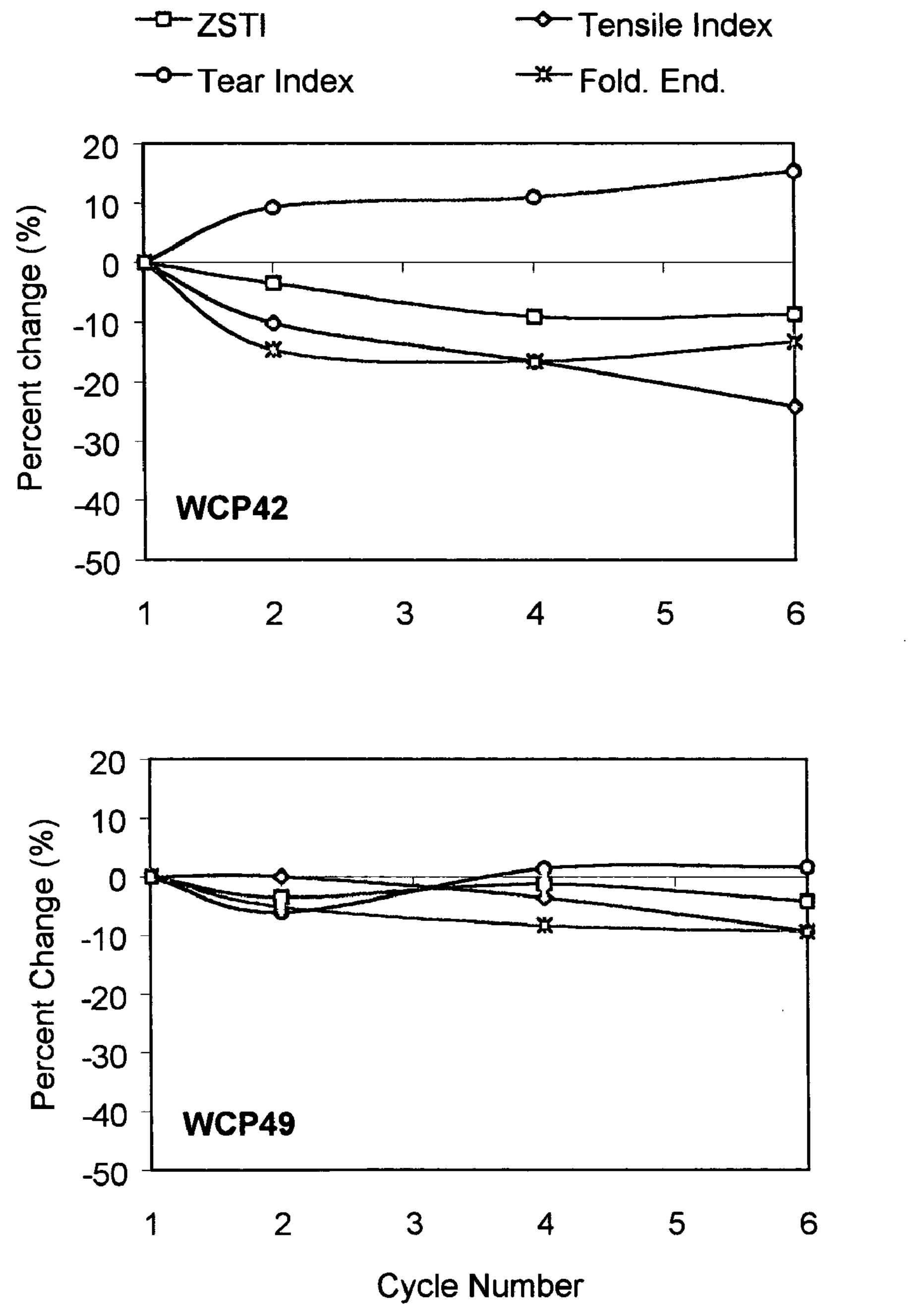

Fig. 4.6: Effect of recycling on strength properties of WCP42 and WCP49 .

Strength Properties

Fig. 4.6 shows percentage changes in tensile index, tear index, zero-span tensile index, and folding endurance as functions of number of recycles for wheat straw chemical pulps. Zero-span tensile index showed a decrease of 8.7% for WCP42 and 4.2% for WCP49 after six cycles.

Tensile index decreases and tear index increases on recycling. These observations are similar to those reported by other workers for chemical wood pulps. However, the magnitude of change is less for wheat straw than for wood pulps reported in the literature (11,12,16,20). Folding endurance also decreases with recycling of these pulps. The change in tensile index, as well as in tear index and folding endurance is more for WCP42 than for WCP49. Both the pulps showed about 20% reduction in burst index after six cycles. (Tables- A2.4 & A2.5, page 137,138)

4.3.3 BAGASSE SEMICHEMICAL PULP

Freeness, WRV, Apparent Density, and Scattering Coefficient

On recycling of semichemical pulp of bagasse pulp, the freeness and the WRV decrease and the scattering coefficient increases as shown in Fig. 4.7. After six cycles, the drop in freeness is 16% and loss in WRV is 28.5%. Increase in scattering coefficient after six cycles is 16%. Changes in apparent sheet density are insignificant.

Bagasse semichemical pulp, Gurley air resistance decreased by about 44% after first cycle and then remained unchanged on subsequent recycling. A similar trend was observed for PS porosity (Table- A2.6, page 139).

Strength Properties

Fig. 4.8 shows percentage change in strength properties for bagasse semichemical pulp during recycling. Repeated recycling results in a reduction of tensile index for bagasse semichemical pulp like it does for chemical pulp of bagasse. However, the

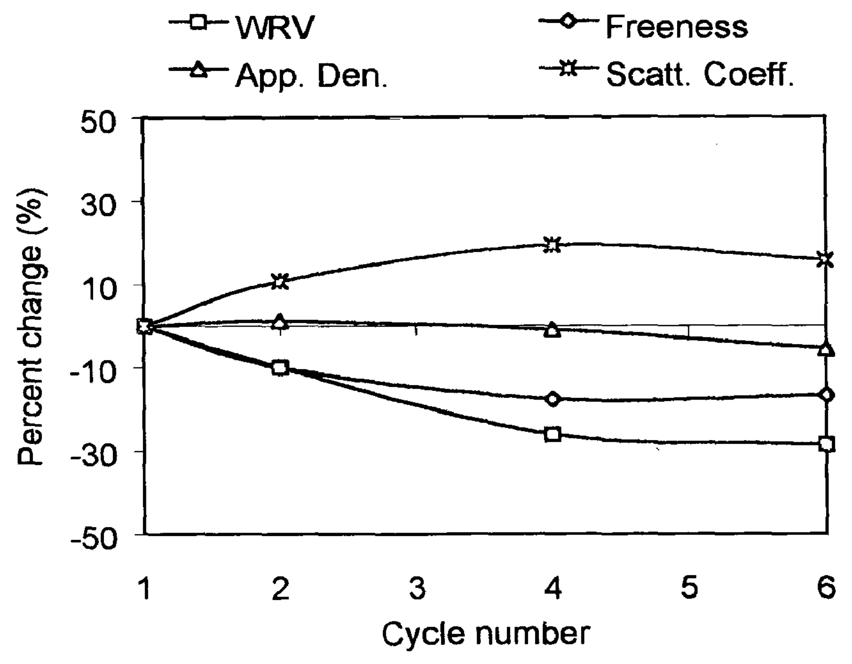

Fig. 4.7: Effect of recycling on physical properties of BSCP65 .

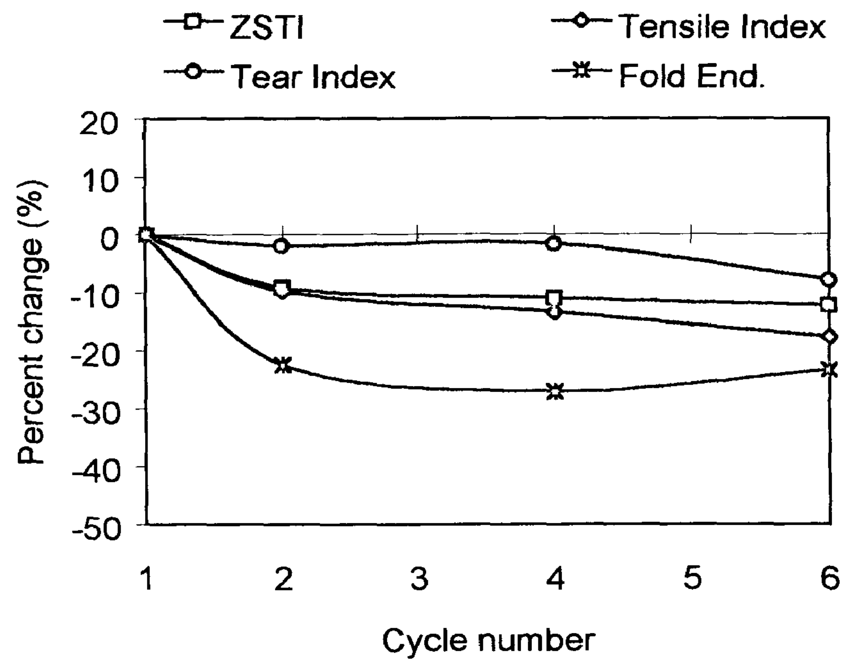

Fig. 4.8: Effect of recycling on strength properties of BSCP65 .

tear index was found to decrease slightly on recycling. A total of 8% reduction in tear index after six cycles has been observed. Zero-span tensile index for bagasse semichemical pulp drops with about 12%, after six cycles (Fig. 4.8). Folding endurance has also dropped by about 20% in six cycles.

Bagasse semichemical pulp has lower values of tensile and burst indices than the values for bagasse chemical pulp. Also the percentage drop in strength of semichemical pulp of bagasse is less than that of its chemical pulp.

4.3.4 WHEAT STRAW SEMICHEMICAL PULP

Freeness, WRV, Apparent Density, and Scattering Coefficient

Effect of recycling of wheat straw semichemical pulp on freeness, WRV, apparent density, and scattering coefficient is shown in Fig. 4.9. These results are similar to the results of wheat straw chemical pulps. Percentage loss in apparent density is small, more or less similar to WCP42 pulp.

The major changes in air resistance, porosity and roughness, have occurred after first cycle. Handsheets show high resistance for air passage in the first cycle. Gurley air resistance in the first cycle has a very high value, more than 12 minutes and value drops to 178 second in second cycle but still higher enough to other pulps in their first cycle. Porosity measurements by PS also show similar findings (Table- A2.7, page 140).

Paper roughness is increased on recycling, as reported in Table- A2.7 (page 140). The handsheets of the first cycle have higher roughness then the chemical bleached pulps of wheat straw.

Strength Properties

Fig. 4.10 shows that strength properties of semichemical pulp of wheat straw change on recycling in a similar manner as those of wheat straw chemical pulps. The percent loss in tensile and burst indices is less than of WCP42. The increase in tear index was found to decrease slightly on recycling. A total of 8% reduction in tear index after six cycles has been observed. Zero-span tensile index for bagasse semichemical pulp drops with about 12%, after six cycles (Fig. 4.8). Folding endurance has also dropped by about 20% in six cycles.

Bagasse semichemical pulp has lower values of tensile and burst indices than the values for bagasse chemical pulp. Also the percentage drop in strength of semichemical pulp of bagasse is less than that of its chemical pulp.

4.3.4 WHEAT STRAW SEMICHEMICAL PULP

Freeness, WRV, Apparent Density, and Scattering Coefficient

Effect of recycling of wheat straw semichemical pulp on freeness, WRV, apparent density, and scattering coefficient is shown in Fig. 4.9. These results are similar to the results of wheat straw chemical pulps. Percentage loss in apparent density is small, more or less similar to WCP42 pulp.

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Paper roughness is increased on recycling, as reported in Table- A2.7 (page 140). The handsheets of the first cycle have higher roughness then the chemical bleached pulps of wheat straw.

Strength Properties

Fig. 4.10 shows that strength properties of semichemical pulp of wheat straw change on recycling in a similar manner as those of wheat straw chemical pulps. The percent loss in tensile and burst indices is less than of WCP42. The increase in

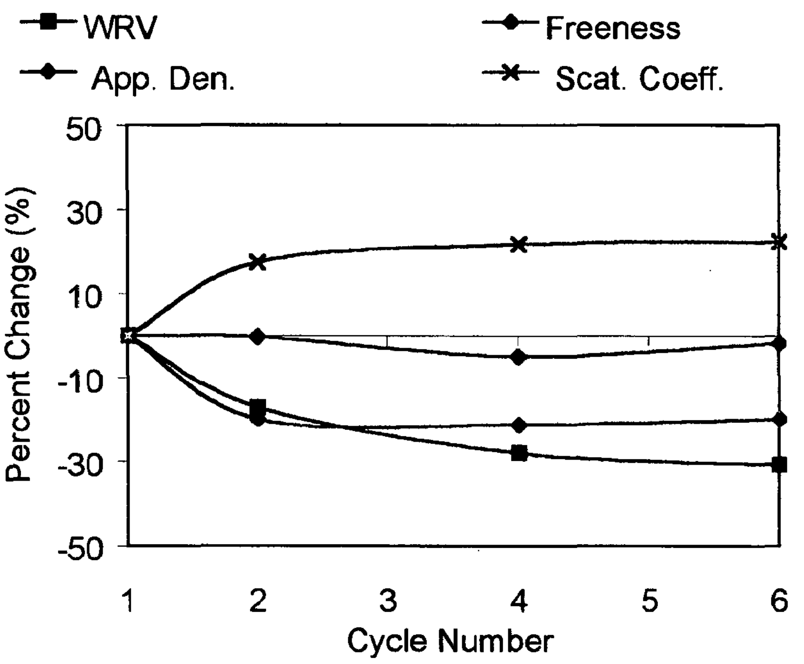

Fig. 4.9: Effect of recycling on Physical properties of WSCP60.

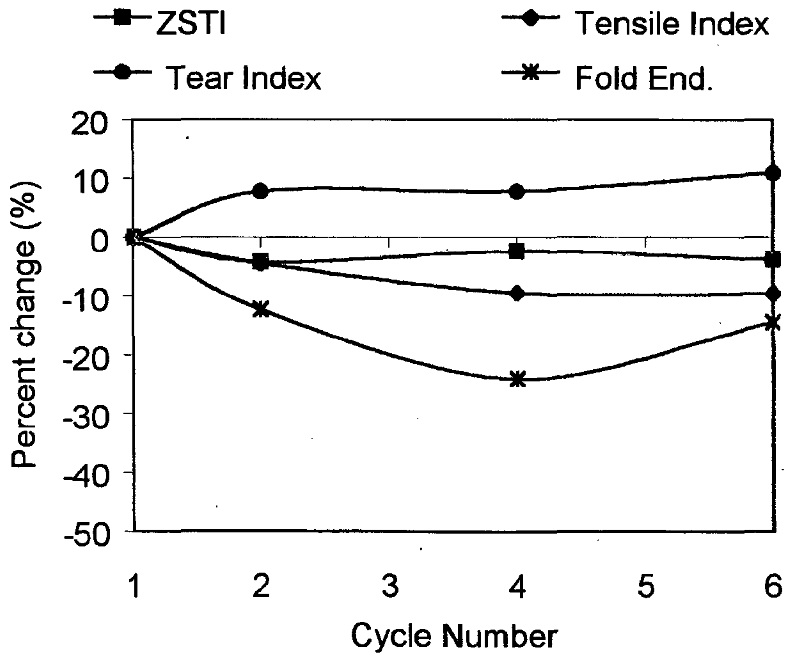

Fig. 4.10: Effect of recycling on strength properties of WSCP60 .

tear index after six cycles is 11%. A small decrease in zero span tensile index was observed after the first cycle.

4.3.5. BAGASSE CHEMIMECHANICAL PULP (CMP)

Bagasse CMP exhibits similar recycling behavior as reported by Law et at. (27) for CMP of aspen.

Freeness, WRV, Apparent Density, and Scattering Coefficient

As shown in Fig. 4.11, freeness of bagasse CMP increases on recycling, about 60% after four cycles. The initial fines content of this pulp is low, which decreases further during recycling. The decrease in WRV is only 6% after fourth and sixth cycles.

Fig. 4.11 shows that the apparent density first decreases slightly in second cycle and then increases by 10.4% in the sixth cycle above the initial value. In opposite, the tensile strength first increases and then decreases by 6.5% in the sixth cycle as shown in Fig. 4.12. Eriksson et al. (29) reported such results for a commercial TMP, density increases and tensile strength decreases on recycling. Similarly scattering coefficient also decreases on recycling of bagasse CMP. The increase in apparent density may cause reduction in scattering coefficient of the hand sheets. It suggests that increase in sheet density and decrease in scattering coefficient not necessarily increases tensile index for CMPs during recycling.

Gurley air resistance for handsheets of all cycles was in the range of 4.5 to 5.5 seconds as given in Table- A2.8 (page 140).

Strength Properties

Fig. 4.12 shows percentage change in strength properties on recycling of bagasse CMP. Zero-span tensile index increases in first cycle and reaches to nearly no change in the sixth cycle. Tensile index shows initial increase and then decreased by 6.5% in the sixth cycle. Burst index is also towards increasing side.

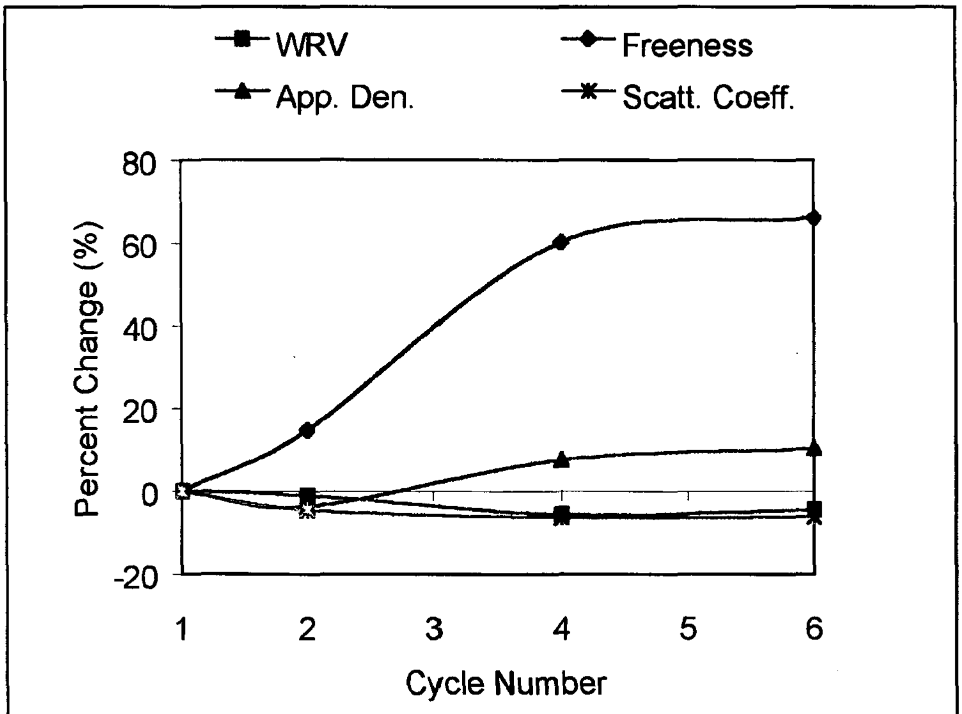

Fig. 4.11: Effect of recycling on physical properties of BCMP .

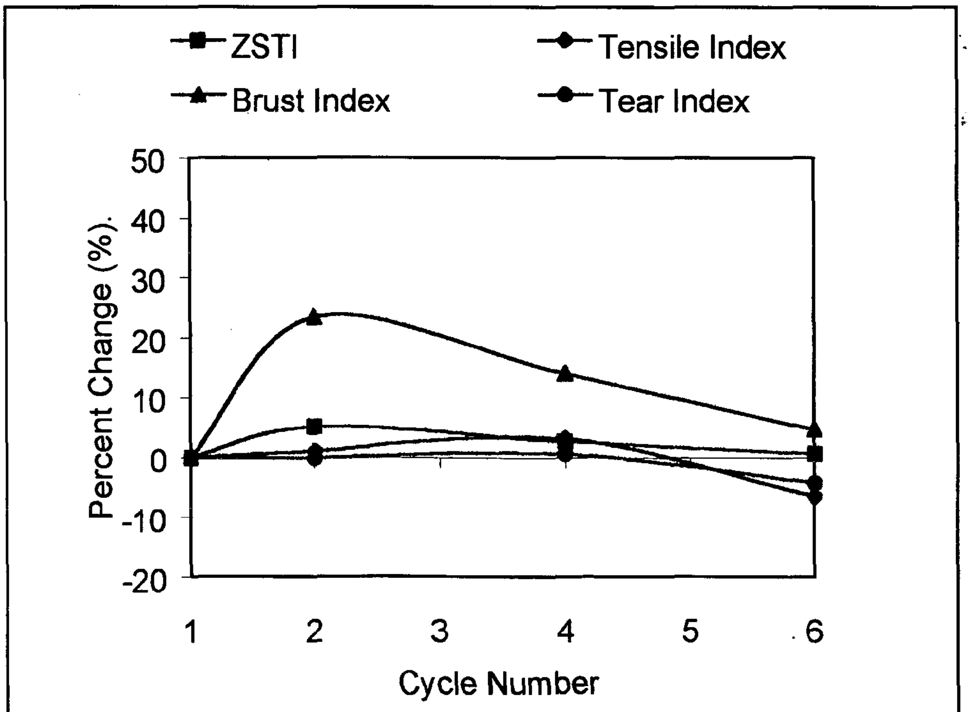

Fig. 4.12: Effect of recycling on strength properties of BCMP .

There was no linear relationship was observed for tensile index with scattering coefficient and WRV, as observed for chemical and semichemical pulps included in this study.

Tear index of the BCMP remained almost unchanged; in the sixth cycle there is slight decrease. The pulp shows zero folding endurance, as the number of double folds is only 1 and 2 at each cycle (Table A2.8, page 140).

These results suggest that although the initial strength level is quite low for bagasse CMP, but it has a better recycling potential than the chemical and semichemical pulps of bagasse.

4.3.6 COMPARISON OF RECYCLING POTENTIAL OF PULPS

Fiber Classification

Bauer-McNett classifications of the six pulps at different stages of recycling are given in Table- 4.1. The fiber classification in the Bauer-McNett classifier is affected by both fiber length and fiber flexibility; short and flexible fibers tend to pass the screen preferentially over long and stiff fibers.

An observation of these data suggests that the recycling potential of a pulp is related with the fines content (P200) in the recycled pulp. For bagasse pulps, the P200 fraction decreases with recycling indicating a loss of fines during sheet making between the cycles. For wheat straw pulps, the P200 fraction remains nearly unchanged on recycling indicating that these fines are capable of retaining in the sheet possibly due to a greater bonding ability than the bagasse pulp fines. This property of wheat straw pulp fines must have been contributing in the higher recycling potential of wheat straw pulps. Similar results have been reported by Aravamuthan and Greaves (8) when they observed an improved recycling potential of softwood fibers when they were mixed with wheat straw fiber in a ratio of 70:30. They noticed that the presence of fines in wheat straw pulp helped in fiber bonding and the wheat straw fibers, inspite of being finer than the softwood fibers, were not preferentially lost in the handsheet making.

Table- 4.1: Effect of recycling on Bauer-McNett classification of pulps.

Pulp Type	Cycle No.	28-Mesh	48-Mesh	100-Mesh	200-Mesh	P200
BCP56	1	20.55	32.02	21.81	11.87	13.75
	2	22.2	33.68	22.00	12.19	9.93
	4	26.04	33.94	21.63	10.23	8.16
	6	-	-	-	-	-
WCP42	1	15.82	34.52	20.8	14.35	14.51
	2	16.06	33.68	19.98	15.02	15.26
	4	16.86	33.82	20.48	15.86	12.98
	6	16.26	34.01	20.02	15.22	14.49
WCP49	1	26.38	31.83	10.04	3.00	28.75
	2	26.43	31.8	12.99	3.65	25.13
	4	25.69	30.12	9.53	5.21	29.45
	6	-	-	-	-	-
BSCP65	1	21.16	22.34	19.86	9.71	26.93
	2	24.08	25.23	15.23	7.03	28.43
	4	-	-	-	-	-
	6	22.07	30.92	23.1	6.91	17.00
WSCP60	1	16.56	25.43	18.9	10.74	28.37
	2	20.39	26.86	20.34	9.54	22.87
	4	22.21	26.51	14.53	8.00	28.75
	6	17.05	28.53	20.3	10.03	24.09
BCMP	1	39.53	28.00	13.37	11.73	7.37
	2	36.82	27.85	13.46	13.77	8.10
	4	40.15	28.98	11.80	14.17	4.90
	6	42.76	29.00	11.07	12.47	4.70

If we discount for the loss of fines during recycling, the fiber classification remains nearly unchanged suggesting that the recycling has no major impact on the fiber length. The literature also suggests that fiber length remains unchanged as the effect of drying-rewetting cycles for wood pulps (Chapter 2, page 8).

Alpha, Beta and Gamma Cellulose

The chemical pulps of wheat straw and bagasse were evaluated for α, β and γ-cellulose contents at first cycle and fourth cycle, as given in Table 4.2. No significant change in α, β and γ cellulose content is observed on recycling of these pulps. The γ cellulose content of the pulp seems to have a profound effect on its recycling potential. The bagasse pulp with lower γ-cellulose content than wheat straw pulps undergoes a greater strength loss on recycling. Cao et al. (7) proposed the following mechanism to explain the role of hemicelluloses in the recycling potential of pulps.

Table- 4.2: Effect of recycling on α, β and γ - cellulose contents of chemical pulps.

	Cycle No.	α-Cellulose	β-Cellulose	γ-Cellulose
WCP42	I	77.96	7.07	14.97
	IV	80.3	5.71	13.99
WCP49	I	77.7	9.4	12.9
	IV	78.50	8.29	13.21
BCP56	I	82.77	11.27	5.96
	IV	81.76	13.73	4.51

Hemicelluloses in both bagasse and wheat straw are mainly pentosans (xylan); hexogens are nearly absent (Table- 1.1, page 3). Cao et al. (7) speculated that for xylan rich pulp, xylan molecules are loosely connected between cellulose microfibrils, forming a barrier between microfibrils. These microfibrils are fairly free from each other (146). As these pulp fibers go from a never-dried water-swollen state to dried state, xylan molecules remain between the cellulose microfibrils and hold them against the tendency to self-associate. Consequently, the cellulose microfibrils remain relatively loose, and upon rewetting, these fibers regain their flexibility. The resultant recycled sheet maintains most of the strength properties of virgin fibers.

Freeness

Freeness of all the wheat straw pulps studied decreases with increased number of recycles (Fig. 4.13). Such a decrease has also been reported for wood pulps. However, bagasse pulps show a different behaviour. A large increase in freeness on recycling of bagasse chemical and CMP pulps is attributable to the loss of fines in the first cycle. Apparently, the pulps (WCP42, WCP49, WSCP60 and BSCP65) having high fines content (P200 fraction) show decrease in freeness during recycling (Table-4.1, page 69).

Water Retention Value

As it is discussed in Chapter 2 (page 20) WRV is a measure of swelling potential of fiber. A reduction in WRV on recycling of fibers points to their hornification. For all the six pulps studied, the value of WRV decreases on recycling. Percentage reduction in WRV increases with number of recycles as shown in Fig. 4.14.

A 15% decrease in WRV after six cycles of WSCP49 pulp was observed. For other chemical and semichemical pulps of wheat straw and bagasse, 30% to 35% reduction in WRV after six cycles was observed. As expected, the loss in tensile and burst indices on recycling of these pulps are different. For bleached sulfate hardwood and softwood pulps, Oye and Yamagishi (16) found a reduction in WRV of 13% after first cycle and the corresponding loss in tensile strength of 60% for hardwood pulp and 49% for softwood pulp. This is also evident from these results that besides WRV, other properties of fiber also control the tensile strength of a

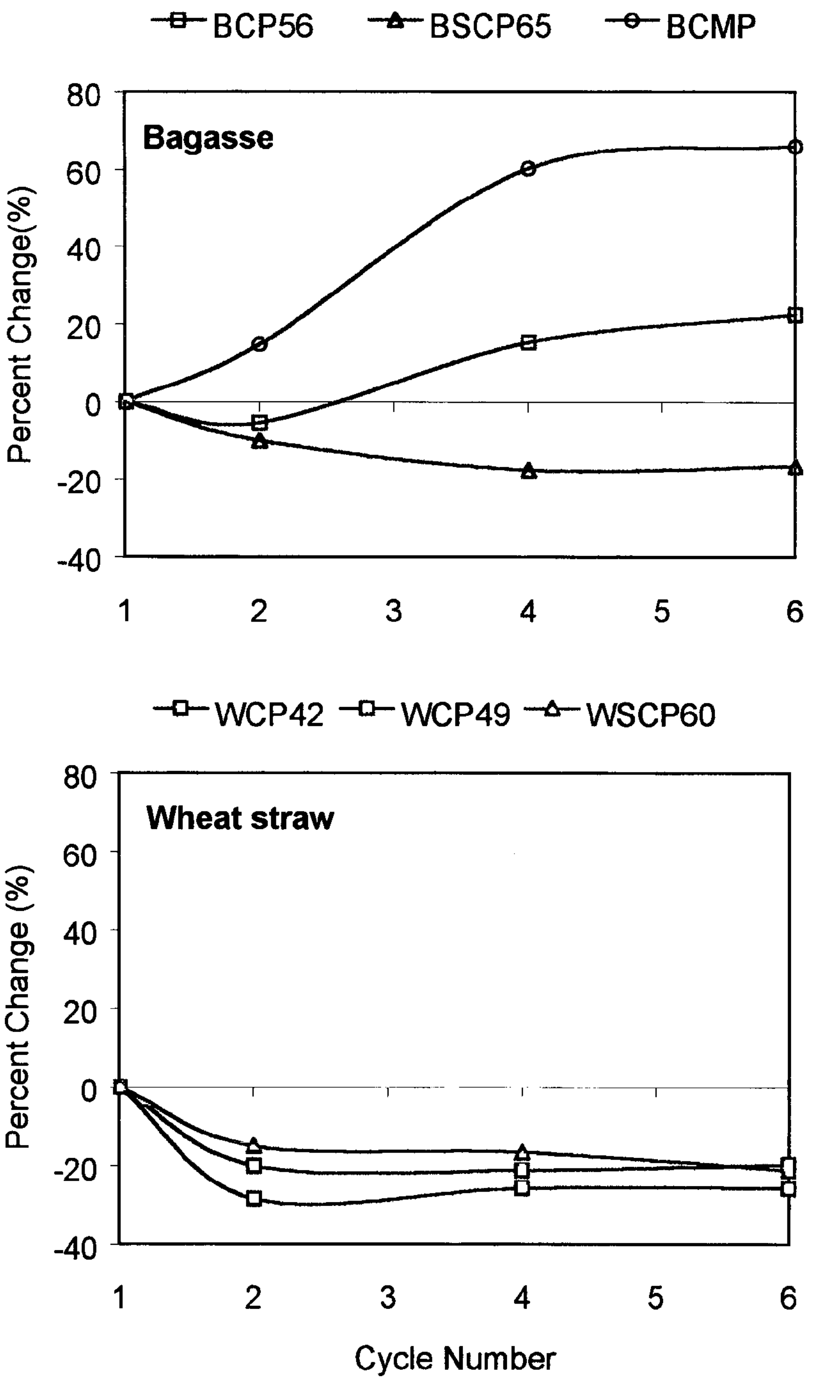

Fig. 4.13: Effect of recycling on freeness of pulps.

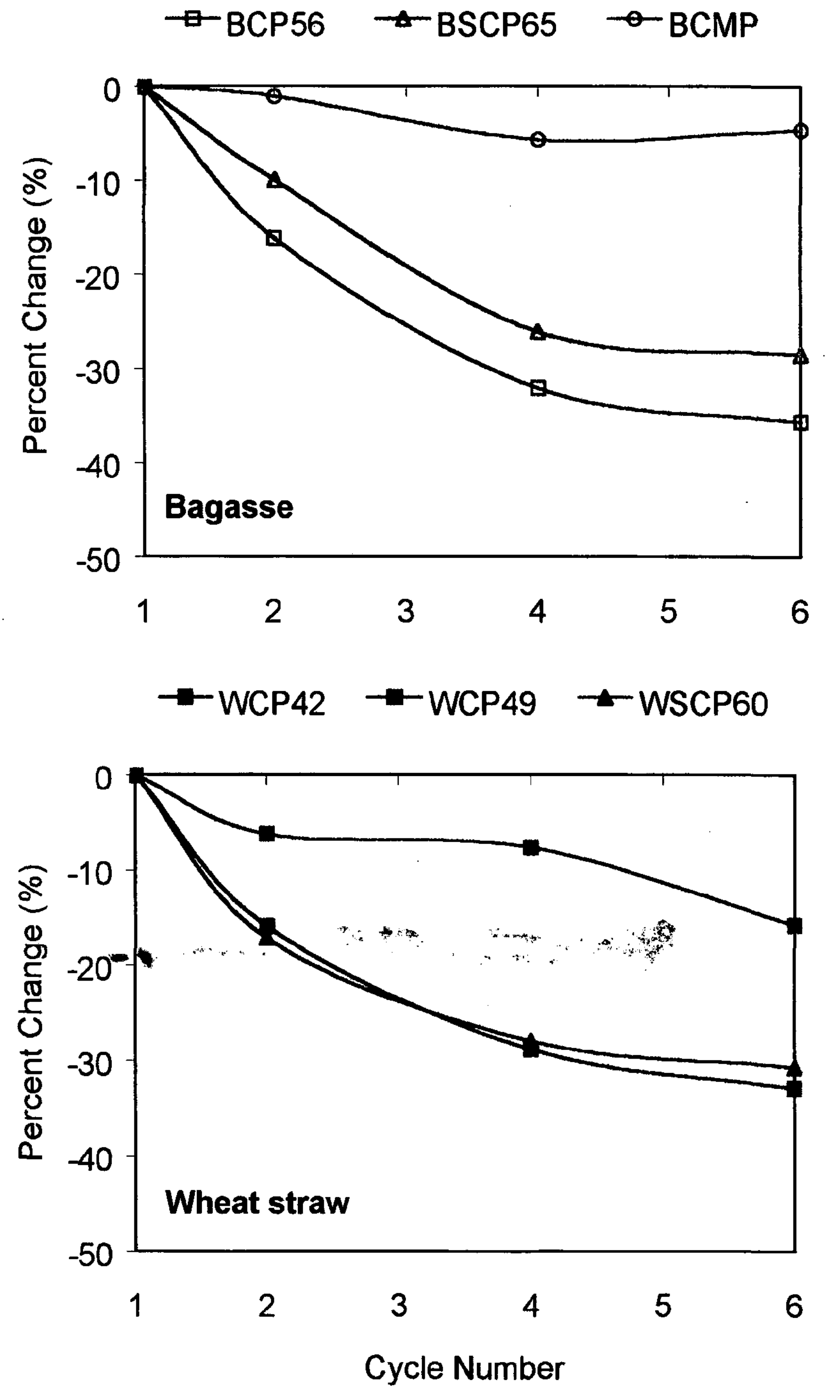

Fig. 4.14: Effect of recycling on WRV of pulps.

sheet. Fibers from different raw materials may have different bonding abilities and the loss in bonding ability during recycling may also be different at same percentage drop in WRV.

Apparent Density

Sheet density and tensile strength of paper decrease on recycling of chemical pulps (Chapter 2, page 9). A drop of 10% to 20% in sheet density after five to six cycles has been reported for softwood and hardwood chemical pulps. As shown in Fig 4.15, apparent sheet density of chemical pulps of wheat straw as well as bagasse decreases on recycling of pulp. The lower is the yield of chemical pulp the greater is the decrease in sheet density. The magnitude of change in sheet density is much less for wheat straw pulps than for bagasse pulps. WSCP49 have observed slight increase or no change in sheet density, though the strength properties are showing a decreasing trend.

Bagasse CMP shows increase in density during recycling even though the tensile index has decreased. This indicates the presence of lignin and hemicelluloses in the pulp preserved during a pulping process, which governs the change in density on recycling of the pulps.

Zero-Span Tensile Index

As shown in Fig. 4.16, zero-span tensile index decreases with recycling for chemical and semichemical pulps of wheat straw as well as bagasse. However, the loss in zero-span tensile strength of wheat straw chemical pulps is less than that of bagasse chemical pulp. This loss decreases as the pulp yield increases for both wheat straw and bagasse. For bagasse CMP pulp, the zero-span tensile index shows an increase on recycling. Other scientists have also observed small increase in zero-span tensile strength for mechanical and chemimechanical pulps (20,27).

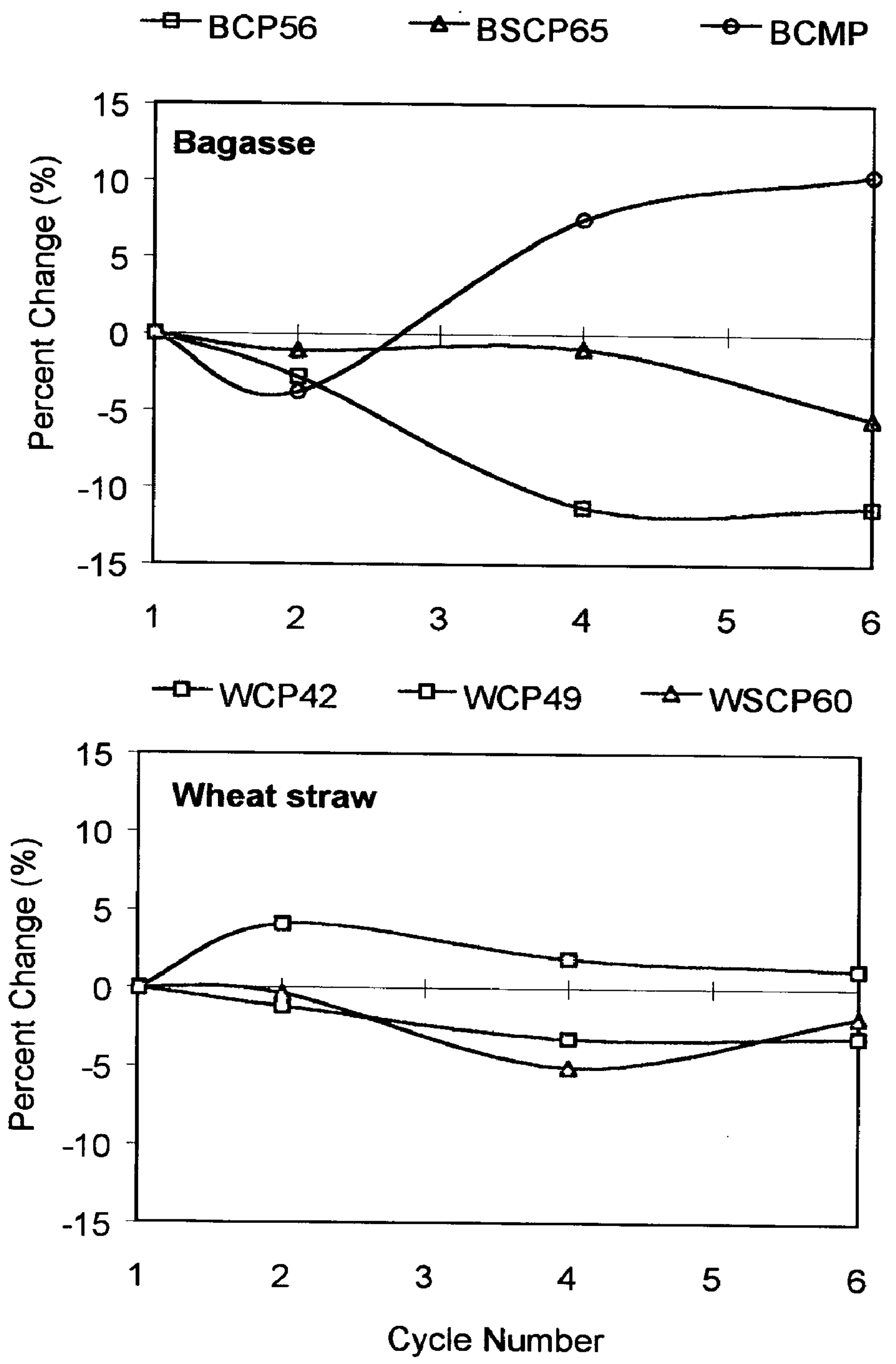

Fig. 4.15: Effect of recycling on apparent density of pulps.

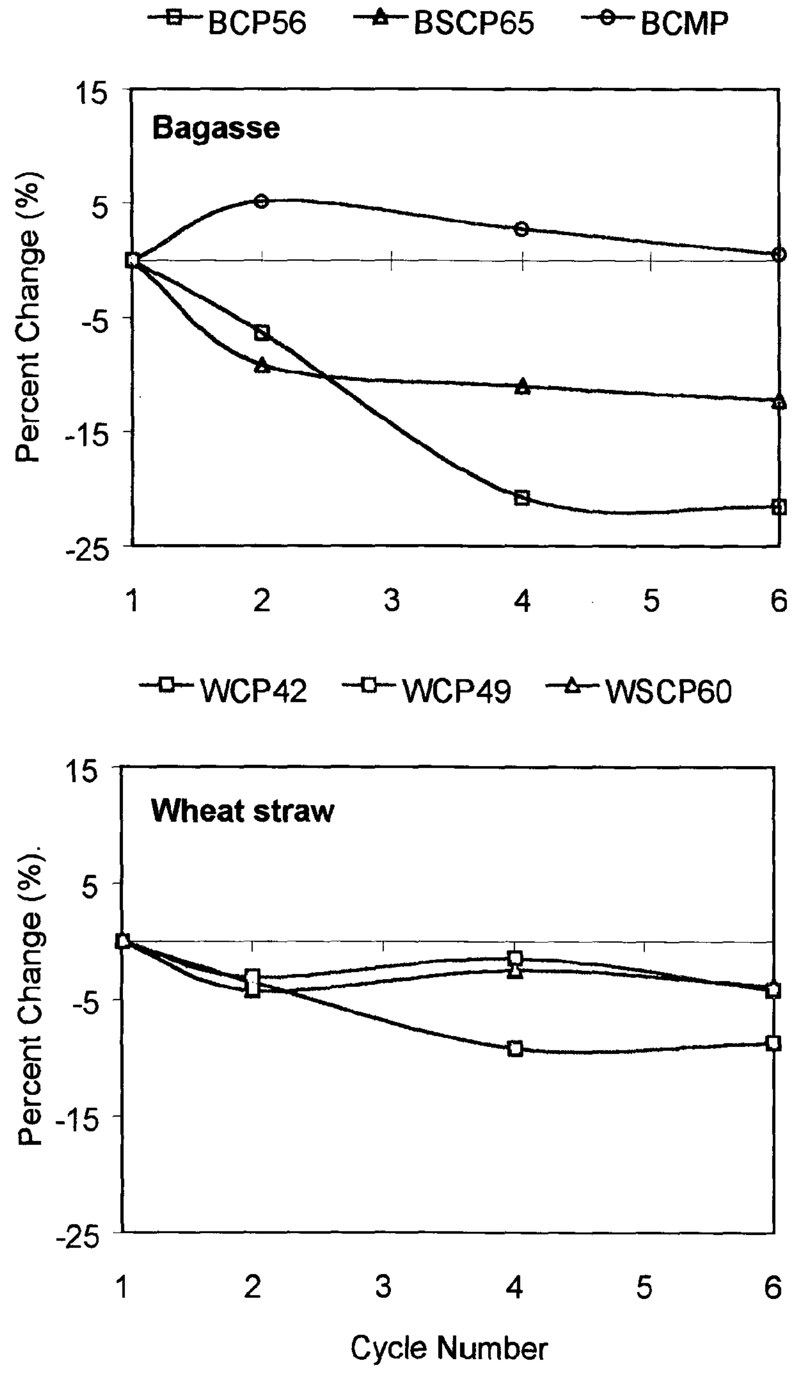

Fig. 4.16: Effect of recycling on zero-span tensile index of pulps.

Boucai (147) has observed that, besides the intrinsic fiber strength, zero-span tensile strength depends on fiber-fiber bonding. Zero-span tensile strength is also dependent on crimps and kinks in the fiber (148,149). We, therefore, cannot say that the change in zero-span tensile strength on recycling noticed in our experiments is due to the loss of fiber strength. The effect of recycling on zero-span tensile strength appears to be high when the changes in fiber bonding and fiber curling are high, for example, for low yield chemical pulps. Low yield pulp fibers are flexible and tend to curl during recycling operations. They also loose their bonding ability to a greater extent than higher yield pulp. On the other hand, high yield pulp fibers are stiffer and have lesser tendency for curl.

Tensile Index

As shown in Fig. 4.17 the tensile index decreases on recycling of pulps. Among the pulps studied here, the loss in tensile index after six cycles is the maximum for bagasse chemical pulp. Wheat straw chemical pulps show less reduction than bagasse chemical pulp. As discussed before, these results agree with the findings of Cao et al. (7). Wheat straw chemical pulps with high γ-cellulose compared with bagasse chemical pulp exhibit lower loss in tensile index. WSCP49 being CEHH bleached (WCP42 is CEH bleached) may contain higher amount of undegraded xylan as hemicelluloses than WCP42, which may have controlled the drop in sheet strength during recycling. As the pulp yield increases, the amount of hemicelluloses content will be more which in turn protect the loss of strength of pulp on recycling. So, for a raw material, as the pulp yield increases the loss in tensile index decreases on recycling. There seems some relation of loss in tensile index with γ-cellulose of chemical pulps.

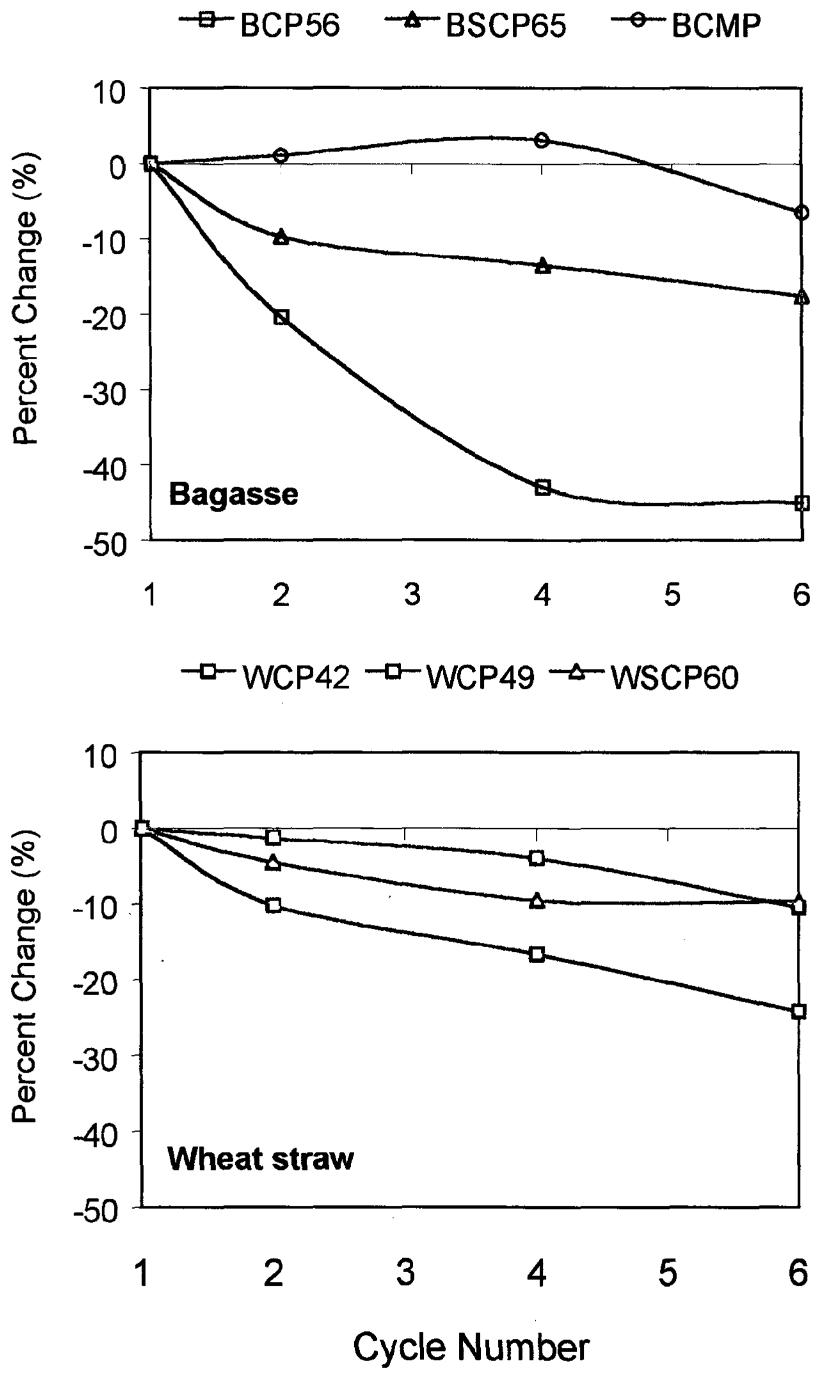

Fig. 4.17: Effect of recycling on tensile index of pulps.

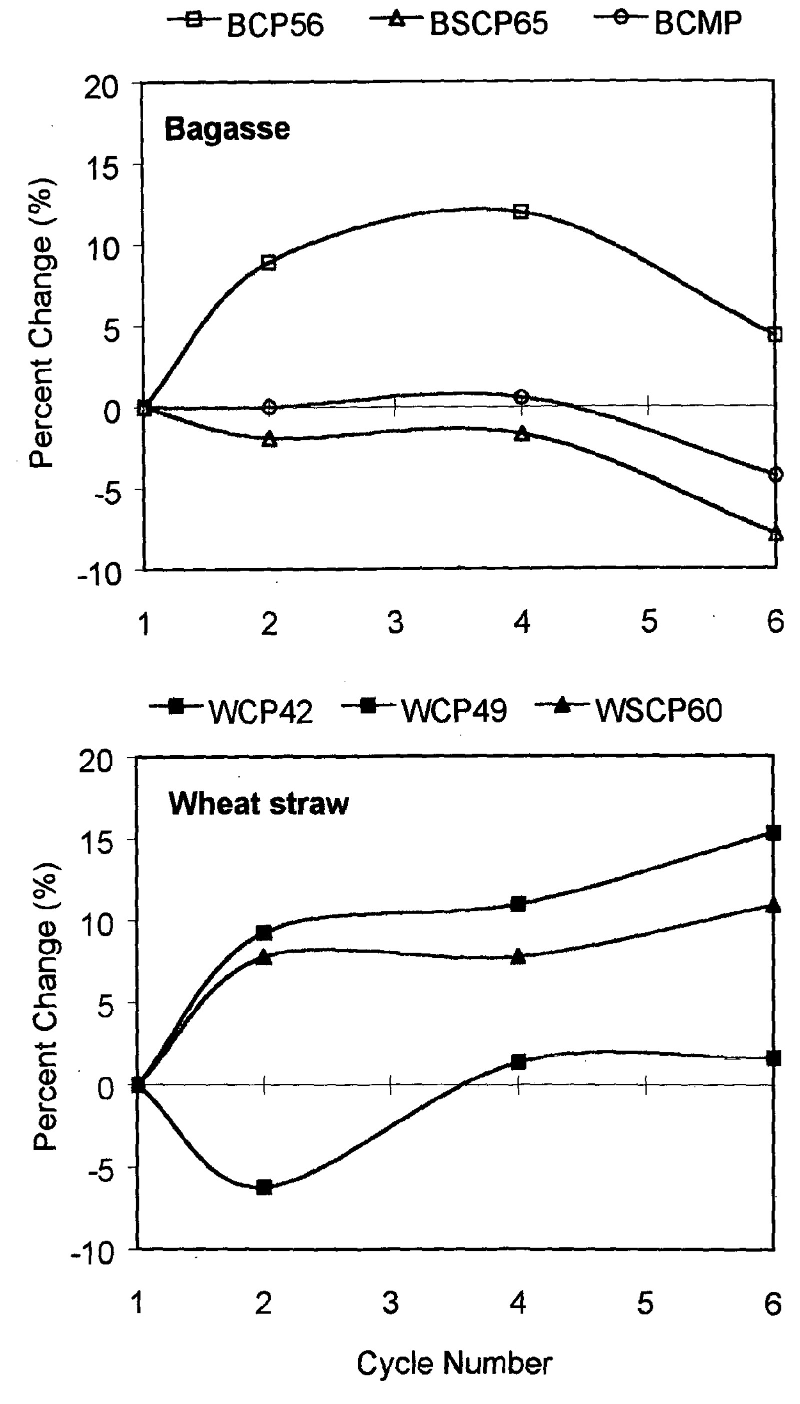

Fig. 4.18: Effect of recycling on tear index of pulps.

Burst Index

The changes in burst index on recycling of pulps are similar to the changes in tensile index. Loss in burst index for wheat straw chemical pulps (20% after six cycles) is less than that for bagasse chemical pulp (60%). Bagasse CMP has observed increase in burst index. The values of burst index at different cycles for the pulps studied here are given in Tables- A2.3 to A2.8 (page 136-140).

Tear Index

Fig. 4.20 shows percentage change in tear index as a function of number of cycles. For some of the pulps the tear index increases with recycling while, for other pulps it decreases or remains unchanged. As enumerated by Seth and Page (38), tear index has a complex relationship with the fiber length, the fiber strength, and the fiber-fiber bonding. As all of these factors are changing in recycling to more or less extent, a generalization on the dependence of tear strength on recycling will be difficult from the data of this study.

The drop in tear index may be due to loss in zero-span tensile index. For well-bonded sheet of paper tear index is proportional to the square of zero-span tensile index (38,39). Zero-span tensile index for bagasse semichemical pulp drops with about 12%, after six cycles (Fig. 4.8).

Other Properties

Changes in some other properties of handsheets of different pulps on recycling are given in Table 4.3.

Air Resistance

Air resistance decreases with recycling for all the pulps studied. Porosity measurement by PS method also exhibits similar results (Tables- A2.3 to A2.8, page 136-140). Howard and Bichard (20) also found decrease in Gurley air resistance. Low yield chemical pulps of wheat straw as well as bagasse show a large decrease in air resistance on recycling. These were pulps that experienced high loss in strength properties. This is consistent with the usual relationship between the tensile strength, the sheet density and the sheet porosity.

Roughness

The results show that roughness of handsheets increases with recycling of pulps. Besides the increase in inter-fiber voids at the paper surface, Klofta and Miller (24) observed that the surface of the fibers themselves became rougher on recycling. The increase in Print-surf roughness at 2MPa clamping pressure seems to be well correlated with decrease in WRV with recycling.

Table- 4.3: Percentage changed in some physical properties on recycling of pulps.

	Cycle No.	**BCP56**	**WCP42**	**WCP49**	**BSCP65**	**WSCP60**	**BCMP**
Air	1	129.3	144.3	77.0	195.0	720.0	04.5
resistance	% Ch (2)	-45.5	-88.8	-11.7	-40.5	-75.3	05.6
(s)	% Ch (6)	-86.5	-90.8	-27.7	-43.6	-80.6	11.1
Roughness	1	4.1	4.2	3.8	5.2	4.4	-
(μm)	% Ch (2)	08.1	05.5	03.3	-	14.1	
20 Kfg/cm^2	% Ch (6)	18.6	19.6	08.5		20.3	
Scattering	1	24.49	35.13	41.75	22.76	17.64	38.85
Coefficient	% Ch (2)	14.2	12.9	03.1	10.6	18.4	-04.6
(m^2/Kg)	% Ch (6)	26.9	23.4	03.6	15.7	23.6	-06.2

Scattering Coefficient

Scattering coefficient increases on recycling of all the pulps except BCMP. The rise in scattering coefficient is due to loss of bonding between fibers during recycling. Fig. 4.21 shows linear relationship between rise in scattering coefficient and loss in tensile strength for all chemical and semichemical pulps of wheat straw and bagasse. WSCP49 has shown very little rise after six cycles and relatively lower loss in tensile index.

Fig. 4.22 shows that there is a linear relationship between scattering coefficient and WRV for all the chemical and semichemical pulps under study.

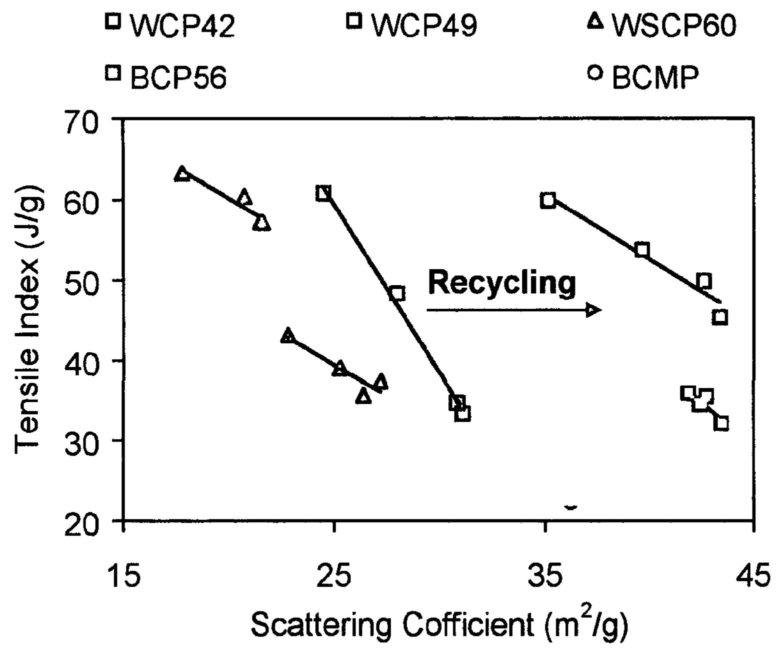

Fig. 4.19: Relationship between tensile index and scattering coefficient of recycled pulps.

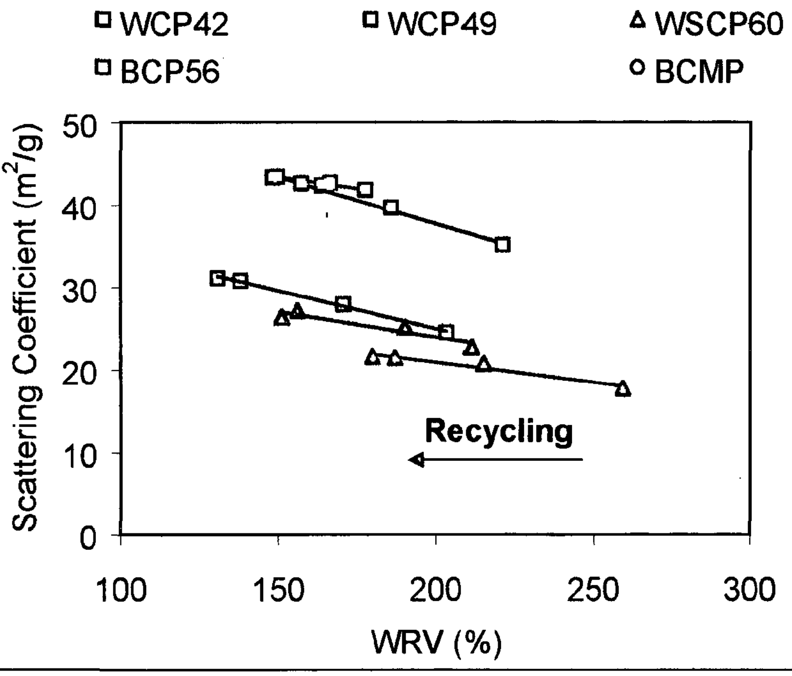

Fig. 4.20: Relationship between Scattering coefficient and WRV of recycled pulps.

4.4 FINDINGS

1. Recycling caused loss in tensile and burst strength of bagasse and wheat straw pulps. The low yield chemical pulps showed a greater loss than the higher yield semichemical pulps. The bagasse CMP showed a minimum change in strength properties. Between the two raw materials bagasse pulps suffered greater loss in strength than wheat straw pulps.
2. The change in tensile and burst indices on recycling of pulps indicates that the wheat straw pulps have a higher recycling potential than the bagasse pulps. The loss in strength of bagasse pulp is of the order of the loss reported for softwood and hardwood pulps.
3. The semichemical pulp of wheat straw showed unusual behaviour. The tensile and burst strength of virgin semichemical pulp of wheat straw were higher than those of chemical pulps. Moreover, these strengths of wheat straw semichemical pulp did not reduce to a large extent on recycling.
4. The recycling potential of the wheat straw semichemical pulp is quite high in comparison to all other pulps.
5. No definite trend is visible for change in tear strength on recycling, for some pulps it increases with recycling while, for others it decreases or remains unchanged. As tear index has a complex relationship with fiber length, fiber strength, and fiber-fiber bonding, and all of these factors are affected on recycling to varying extents, a generalization on the dependence of tear strength on recycling has been difficult.
6. Fiber classification (Bauer-McNett) remains nearly unchanged on recycling of wheat straw pulps, but shows a high loss of fines (P200) fraction on recycling of bagasse pulps. A loss of 40% to 50% of P200 content present in virgin pulp was observed for all the bagasse pulps included in this study.

7. There appears no major impact of recycling on the fiber length.
8. The proportions of alpha, beta, and gamma cellulose do not change with recycling of bagasse and wheat straw pulps.
9. Bagasse chemical pulps suffer a greater loss in tensile and burst strength than do the wheat straw chemical pulps. This could be due to lower gamma cellulose content in bagasse pulp.
10. The effect of recycling on pulp freeness appears to depend on the fines content present initially in the pulp. Freeness of wheat straw pulps and semichemical pulp of bagasse decreased with recycling, while, freeness of bagasse CMP and chemical pulp increased with recycling.
11. Fiber swelling, measured in terms of WRV, decreased with recycling of all types of bagasse and wheat straw pulps studied. A gradual reduction in WRV up to six cycles was observed for these pulps, unlike wood pulps where the major loss in fiber swelling is reported to occur in the first cycle.
12. A certain reduction in WRV does not indicate a reduction in tensile or burst strength to the same extent for all the pulps. Clearly, WRV is a good measure of fiber swellability, but not of strength of the paper.
13. On recycling, apparent sheet density decreases for bagasse chemical pulps, but increases to some extent for bagasse CMP. The lower the yield of pulp the greater is the decrease in sheet density. The magnitude of change in sheet density is much less for wheat straw pulps than for bagasse pulps.
14. A greater linear correlation between tensile index and apparent density exists for lower yield pulps than for higher yield pulps.
15. Recycling appears to affect zero-span tensile strength of pulps. A decrease in zero-span tensile strength was observed for chemical and semichemical pulps, the bagasse pulps showing a greater change than the wheat straw pulps. The

lower the yield of pulp the greater was the loss in zero-span strength. For bagasse CMP, the zero-span tensile index showed an increase on recycling. As pointed out by Seth (149), the change noticed in zero-span tensile strength could be due to changes in fiber curling for low yield chemical pulps rather than to the intrinsic fiber strength.

16. Air resistance showed a decrease with recycling for all the pulps studied. Low yield chemical pulps of wheat straw as well as bagasse showed a large decrease in air resistance on recycling.
17. For all pulps roughness of handsheets increased with recycling.

CHAPTER 5

RESPONSE OF RECYCLED PULPS TO REFINING

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RESPONSE OF RECYCLED PULPS TO REFINING

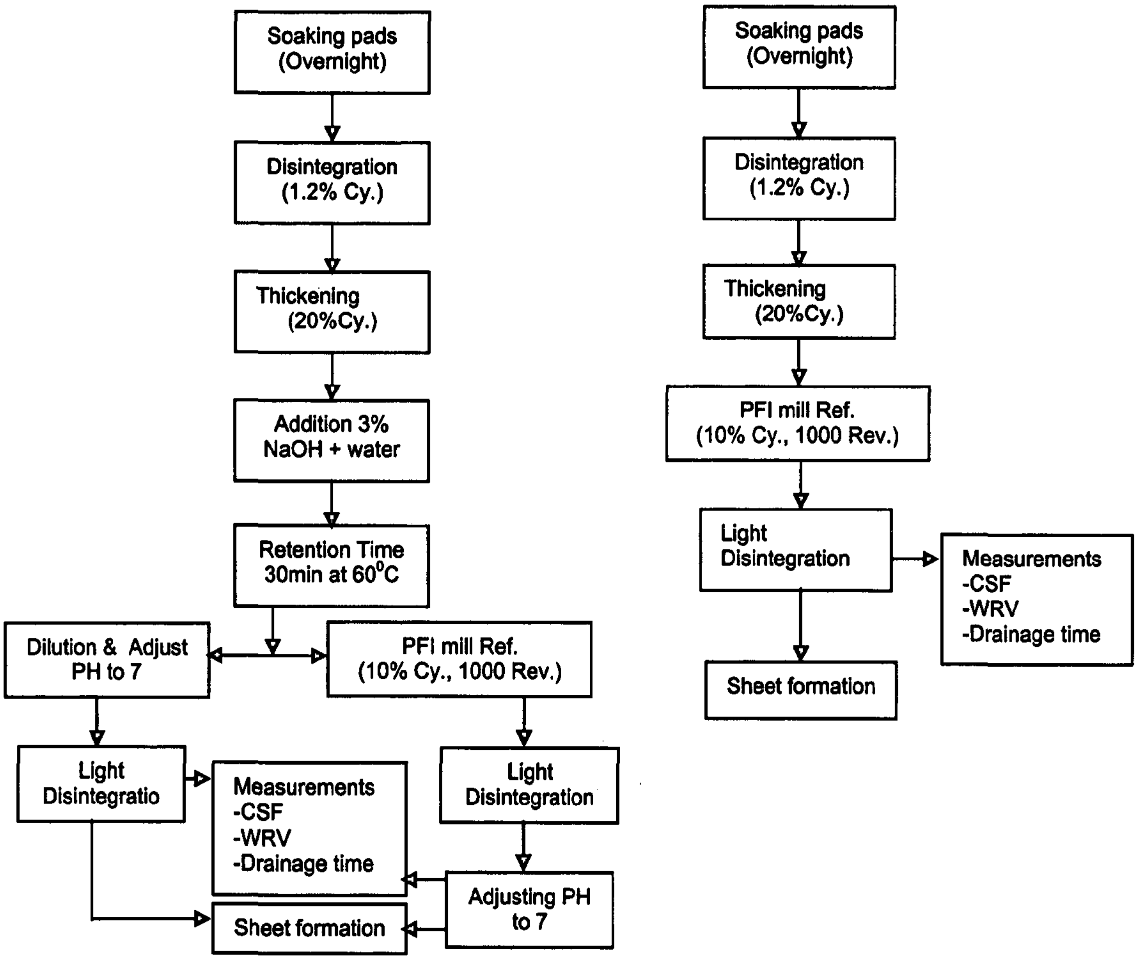
5.1 INTRODUCTION

In this part of the study, response of bagasse and wheat straw recycled chemical pulps to conventional strength enhancement treatments has been evaluated. Response to strength enhancement methods is an important component of overall recycling potential of a pulp, and is helpful in optimizing the use of recycled fiber. The recycled pulps were subjected to alkali treatment, refining, and combination of both. For some experiments, the pulps were fractionated into a fine and coarser fractions, and the coarser fraction was refined separately and mixed back with the fines. Physical and strength properties of the treated pulp have been compared with the properties in untreated recycled and virgin state. Freeness of the recycled pulps decreases sharply on refining. Reduction in freeness due to refining is more severe for wheat straw pulps. Very fine particles (P250) contribute to a great deal in the slowness of the wheat straw pulp, as indicated by a significant rise in freeness when this fraction was removed from the pulp.

5.2 EXPERIMENTAL PLAN

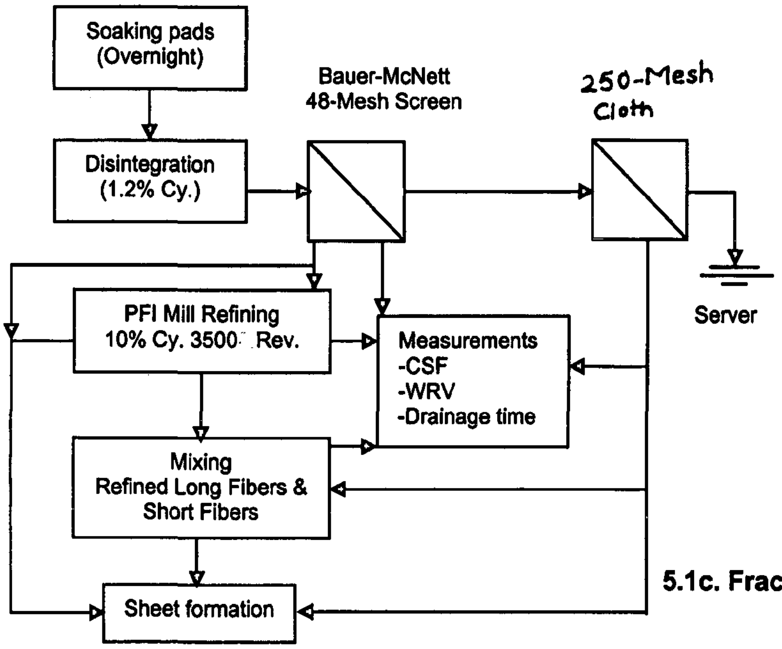
Bleached chemical pulps of bagasse and wheat straw, namely, BCP56 and WCP49, were used to study the effect of various mechanical and chemical treatments between the cycles on the properties of handsheets. Pulp pads prepared after first, second and fourth cycle were used for this study.

The experiments conducted have been shown diagrammatically in Fig. 5.1. Pulp pads were soaked in water overnight and disintegrated in a laboratory disintegrator at 1.2% consistency. The disintegrated pulps were subjected to one of the following treatments:



5.1a. Alkali Treatment and Alkali Plus Refining Treatment

5.1b. Refining



5.1c. Fractionation

Fig. 5.1: Experimental Procedure for four treatments applied on recycled pads.

1. Refining in a PFI mill for 1000 revolutions (Fig. 5.1a)
2. Alkali treatment with 3% NaOH on o.d. pulp basis at 10% consistency for 30 min at 60^0C. Stock neutralized before sheet making. (Fig. 5.1b)
3. Alkali treatment followed by refining in the alkaline conditions. (Fig. 5.1b)
4. Fractionation using a Bauer-McNett classifier: Separation of +48 mesh fraction, refining it in a PFI mill for 3500 revolutions, and mixing it with the separated short fiber fraction (Fig. 5.1c).

   Gooding and Olson (150) have shown analytically that the BMC classifies fibers mainly by length. The degree of fractionation in a BMC is comparable to that found in industrial pressure screens and it can be used as a device to explore the fundamentals of fractionation.

Handsheets were prepared from untreated and treated pulps. CSF, WRV and drainage time were determined for pulps. Physical properties of handsheets were evaluated using standard methods as mentioned in Table- A2.1 (page 134).

For fractionation of BCP56, pads of cycle 2 and 5 were used and for fractionation of WCP49 pads of cycle 1 and 2 were used. The fractionation was done in a Bauer Mc-Nett classifier using 48-mesh (320 μm) screen. The fraction passing through 48-mesh screen (P48 fraction) was screened over a filter cloth of 250-mesh. The fraction retained on 48-mesh screen (R48) was refined in a PFI mill for 3500 revolutions and was mixed with the P48/R250 fraction in a 1:1. It was called "fractionated mixed pulp" (FMP). The recycled stocks are also fractionated on 100-mesh screen to compare the properties of the long fibers separately collected on 48 and 100-mesh screens.

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT ON PHYSICAL PROPERTIES

Freeness and Drainage Time

Table 5.1 shows freeness and drainage time at different cycles for untreated pulps and treated pulps. The percentage change in freeness of the treated pulp over the untreated pulp for a given cycle number has also been shown. The freeness and drainage time follow the same trend for the pulps used in this study. Alkali treatment increases freeness for both BCP56 and WCP49 pulps. Increase in freeness on alkali treatment of OCC furnish is reported in literature (101,102).

Refining of recycled pulps for 1000 revolutions in PFI mill shows a reduction of about 35% in the freeness of untreated pulp. This appears very severe for wheat straw pulps since their freeness decreases considerably during recycling. Refining after alkali treatment of pulps causes less decrease in freeness for the same number of revolutions in PFI mill.

The results of fractionation experiments are influenced to some extent by the loss of very fine particles through the filter cloth (P250). The loss of P250 fraction during fractionation was about 12% for wheat straw recycled pulps and about 8% for bagasse recycled pulps.

As expected, the freeness of coarser fractions, R48 and R100, are greater than the freeness of fines fractions (P48/R250) for both the pulps. The freeness of fines fraction is slightly less than the whole pulp for recycled pulp of bagasse, but it is approximately 60% more than the whole pulp for recycled pulp of wheat straw. Although the freeness of whole recycled pulp of bagasse is more than that of wheat straw, the P48/R250 fractions of both the pulps have nearly the same freeness. Apparently, the slowness of the wheat straw pulp is contributed to a great deal by the P250 fraction.

Table- 5.1: Effect on freeness of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56)			Wheat straw (WCP49)		
		CSF (ml)	%Change in CSF	Drainage Time (s)	CSF (ml)	%Change in CSF	Drainage Time (s)
Initial value	1	335		7	334		8.5
Untreated	2	317		9	235		10.5
	3	370		9	240		10.5
	5	392		9	250		10.5
Alkali treated	2				259	10.21	10
	3	433	17.03	9	259	7.92	10.25
	5	455	16.07	9	277	10.80	10
Refined	2				149	-36.60	28
	3	230	-37.84	21.25	155	-35.42	29
	5	258	-34.18	22	155	-38.00	29
Alkali treated plus Refined	2				161	-31.49	24
	3	281	-24.05	19.5	177	-26.25	25
	5	295	-24.74	19.5	192	-23.20	25
R48 Fraction	2	610		7	500		7.5
	3	604		7	500		7.5
	5	589		7	515		7.5
R100 Fraction	2	552		7	544		7.25
	3	610		7.25	503		7.5
	5	558		7	468		7.5
Fines Fraction P48/R250	2				391	66.38	16
	3	352	-4.86	16.5	385	60.42	16
	5	332	-15.31	18			
Refined R48 Fraction	2				386	22.80	9
	3	402	-33.44	8	357	28.60	9.25
	5	425	-27.84	8.25			
Fractionated Mixed Pulp (FMP)	2				343	45.96	9.5
	3	395	6.76	9	314	30.83	9.5
	5	407	3.83	9			

The R48 fractions could be refined more intensely without much drop in freeness. The freeness values of R48 fraction after 3500 revolutions in PFI mill of wheat straw and bagasse pulps are given in Table-5.1. The freeness values of fractionated mixed pulps are much greater than the refined whole pulps for both wheat straw and bagasse recycled pulps. The freeness of the mixture of refined R48 fraction and fines fraction in a 1:1 ratio is different from a weight mean freeness of the two fractions.

Water Retention Value (WRV)

Fig. 5.5 shows WRV plotted as a function of number of cycles for various treated pulps. The WRV of recycled pulp always remains less than the WRV of virgin pulp for both the pulps for all the treatments undertaken in this study. WRV at different cycles for untreated and treated recycled pulps and their fractions are reported in Table- A3.1 (page 141). The percentage changes in WRV of the treated pulp over the untreated pulp at different cycles are also given in the Table- A3.1 (page 141).

During recycling, the drop in WRV of bagasse pulp (BCP56) is considerably more than the drop in WRV of wheat straw pulp (WCP49). The methods of treatment used in this study affect very little the WRV of recycled wheat straw pulp. Alkali treatment alone does not increase the WRV for these bleached chemical pulps as reported for wood pulps in the literature (64,105,106). For bagasse pulps, refining, without or with alkali treatment, could be used to recover partly the loss in WRV due to recycling.

The WRV of the coarser fractions (R48 and R100) of the recycled pulps is less than the WRV of the fines fraction. Incidentally the WRV of coarser fractions of both the pulps are nearly same, and the difference between the two pulps arises because of difference in WRV of fines fractions. Mixing of refined R48 and

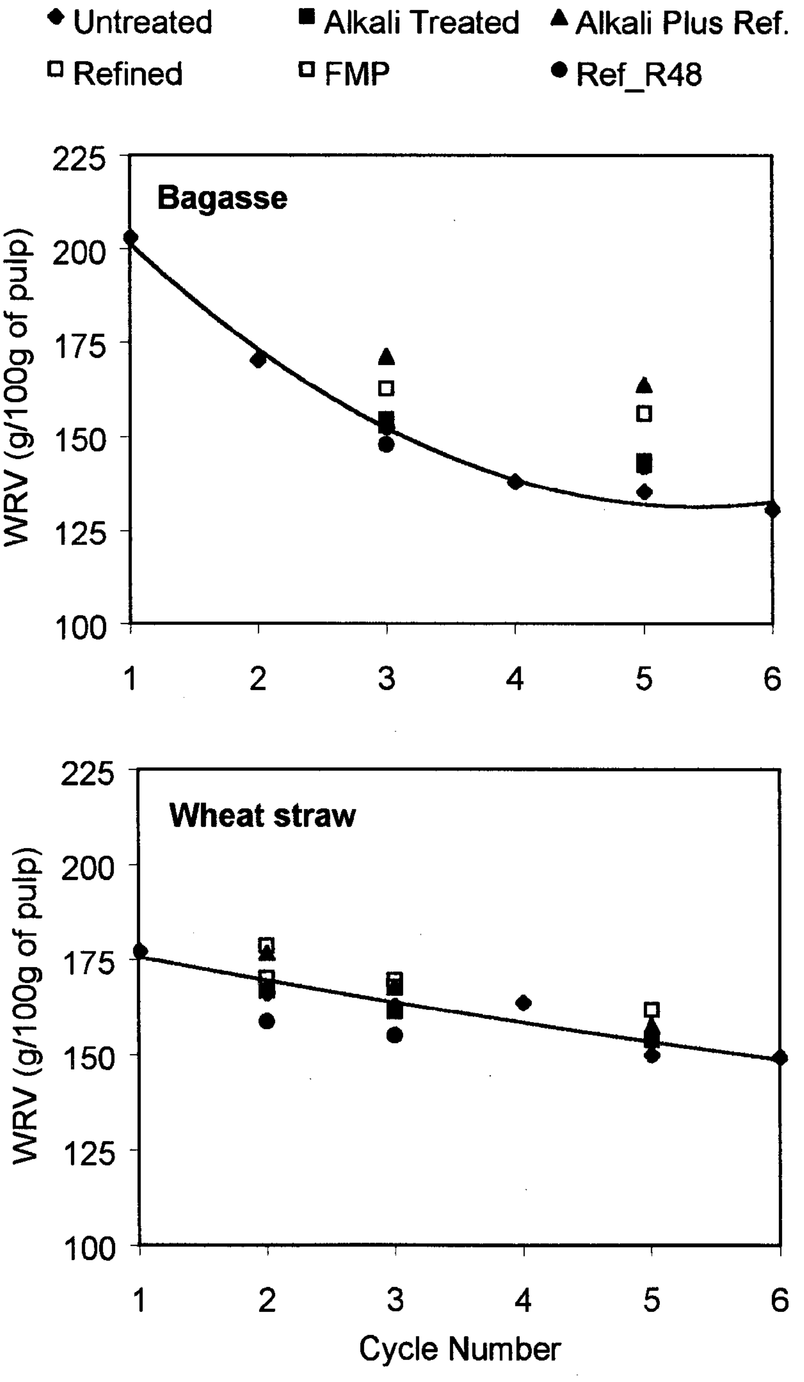


Fig. 5.2: Effect on WRV of various treatments on recycled pulps.

P48/R250 fractions in 1:1 ratio (fractionated mixed pulp) did not give any significantly greater WRV than that of refined whole pulp. It may be recalled that the R48 fraction is refined for 3500 revolutions and whole pulp is refined for 1000 revolutions in PFI mill.

Apparent Density

Apparent density of a sheet is considered as an important tool for comparing strength properties and fiber bonding (151,152). Fig. 5.6 shows the effect of different treatments on the apparent density of bagasse and wheat straw pulps. Alkali treatment alone does not cause large changes in sheet density of both bagasse and wheat straw recycled pulps. Refining with and without alkali treatment of recycled pulps increases sheet density nearly to the same order. Fractionated mixed pulp of bagasse-recycled pulp gives a high sheet density at a relatively higher freeness compared with other treatments. The experimental data along with percentage change are given in Table- A3.2 (page 142).

Air Resistance

Air resistance of sheets is measured by Gurley method, as given in Table 5.2. No major changes in air resistance are observed due to alkali treatment of both bagasse and wheat straw recycled pulps. Refining, without or with alkali treatment, increases air resistance consistent with the increased sheet density. Increase in the air resistance of wheat straw pulp is much more than that of bagasse pulp.

Sheets made from the fines fractions (P48/R250) of wheat straw pulp have higher air resistance than those made from the fines fraction of bagasse pulp. Sheets made of R48 fractions of both the pulps have very low air resistance and have nearly same values. Refining of R48 fraction results in nearly same increase in air resistance for both bagasse and wheat straw pulps. Mixing refined R48 fraction with fines fraction (fractionated mixed pulp) shows higher air resistance for

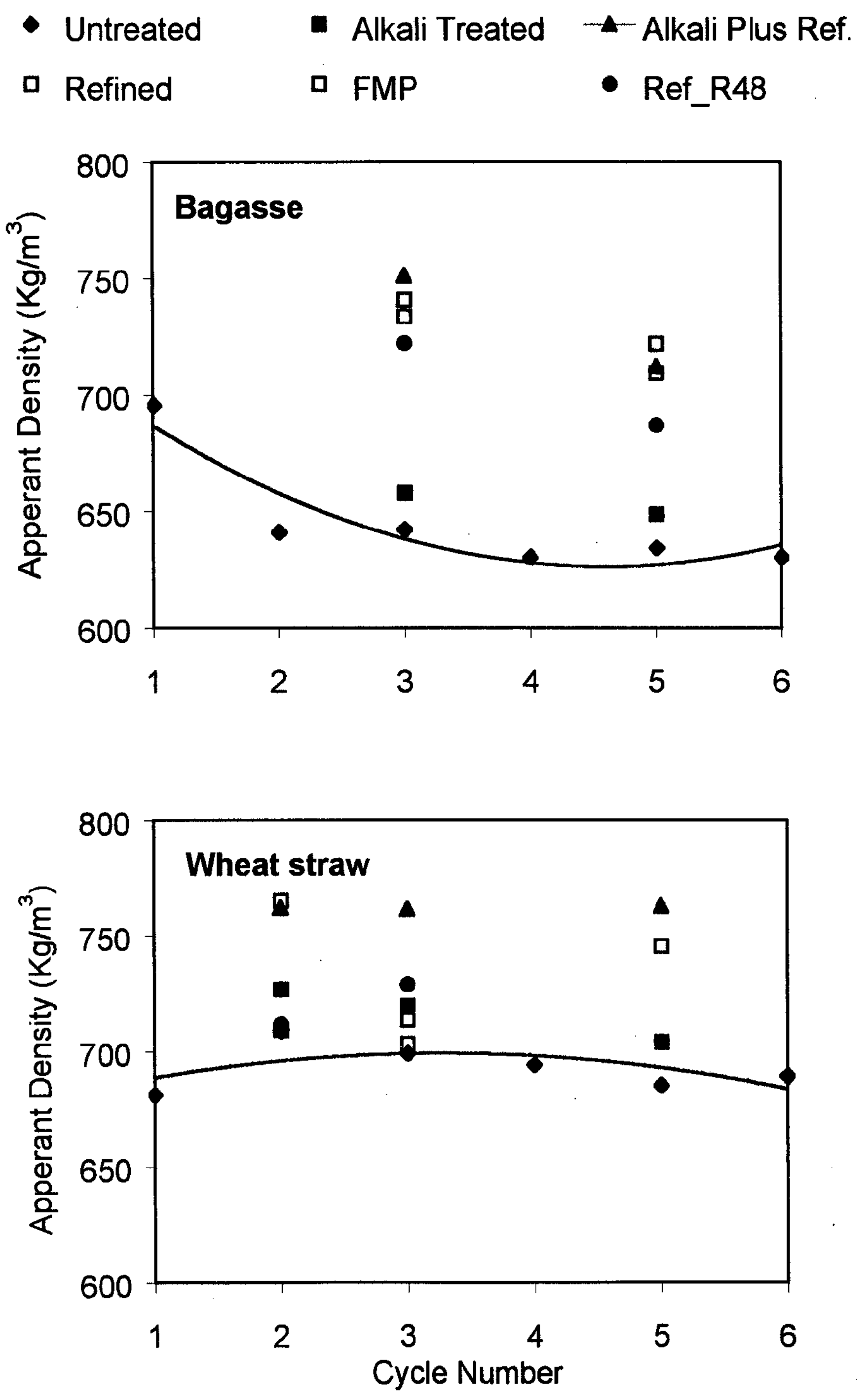


Fig. 5.3: Effect on apparent density of various treatments on recycled pulps.

Table- 5.2: Effect on air resistance of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56)		Wheat straw (WCP49)	
		Air Resis. (s)	% Change	Air Resis. (s)	% Change
Initial value	1	129.25		77.00	
Untreated	2	70.5		66.00	
	3	35.14		69.00	
	5	20.00		58.00	
Alkali treated	2			77.00	16.67
	3	26.60	-24.30	90.00	30.43
	5	36.00	80.00	54.00	-6.90
Refined	2			280.00	324.24
	3	150.00	326.86	275.00	298.55
	5	140.00	600.00	280.00	382.76
Alkali treated plus Refined	2			360.00	445.45
	3	140.00	298.41	240.00	247.83
	5	120.00	500.00	192.00	231.03
R48 Fraction	2	7.00		5.00	
	3	7.00		5.00	
	5	7.00		10.00	
R100 Fraction	2	7.00		8.00	
	3	7.00			
	5	7.00		11.00	
Fines Fraction P48/R250	2			150.00	127.27
	3	92.00	-28.85		
	5	62.00	-52.05		
Refined R48 Fraction	2			30.83	516.60
	3	24.50	250.00	26.67	433.40
	5	15.00	114.29		
Fractionated Mixed Pulp (FMP)	2			67.00	1.52
	3	39.00	10.98	71.00	2.90
	5	29.50	47.50		

Table- 5.3: Effect on roughness of various treatments on recycled pulps.

Treatment	Cycle No.	Print-surf roughness (μm)							
		Bagasse (BCP56)				Wheat straw (WCP49)			
		Clamp pressure (MPa)		% Change		Clamp pressure (MPa)		% Change	
		0.5	20	0.5	20	0.5	20	0.5	20
Initial value	1	5.10	4.09			4.15	3.31		
Untreated	2	5.78	4.42			4.29	3.51		
	3	>6	4.61			4.69	3.56		
	5	>6	4.82			4.78	3.55		
Alkali treated	2					4.47	3.52	4.20	-5.13
	3	5.79	4.49		-2.60	4.06	3.33	-13.43	-1.12
	5	5.67	4.42		-8.30	4.47	3.34	-6.49	-5.92
Refined	2					4.72	3.62	10.02	3.13
	3	5.56	4.65		0.87	5.14	3.62	9.59	1.69
	5	5.91	4.72		-2.07	4.43	3.47	-7.32	-2.25
Alkali treated plus Refined	2					4.48	3.43	4.43	-2.28
	3	5.35	4.22		-8.46	4.68	3.42	-0.21	-3.93
	5	5.51	4.25		-11.83	4.61	3.54	-3.56	-0.28
R48 Fraction	2	>6	5.14			4.86	3.77		
	3	>6	5.36			5.08	4.21		
	5	>6	5.48			5.27	4.03		
R100 Fraction	2	>6	5.22			5.05	4.03		
	3	>6	5.20						
	5	>6	5.63			5.00	3.99		
Fines Fraction P48/R250	2					3.63	2.87		
	3	4.68	3.64						
	5	4.84	3.68						
Refined R48 Fraction	2					4.47	3.59	-8.02	-4.77
	3	5.60	4.70		-12.31	4.65	3.55	-8.46	-15.68
	5	>6	4.93		-10.04				
Fractionated Mixed Pulp (FMP)	2					4.16	3.44	-3.03	-1.99
	3	5.41	4.28		-7.16	3.62	3.09	-22.81	-13.20
	5	5.48	4.41		-8.51				

wheat straw pulp than for bagasse pulp. This indicates that the fines fraction of recycled wheat straw chemical pulp has a better bonding potential than fines fraction of recycled bagasse chemical pulp.

Roughness

Recycling causes an increase in Print-surf roughness of handsheets of both bagasse and wheat straw pulps. Treatments on the recycled pulps carried out in the present study do not show any major change in the roughness of handsheets (Table 5.3). Roughness of handsheets made from bagasse recycled pulp remains greater than the roughness of handsheets made from wheat straw pulp for both coarse and fine fractions.

Scattering Coefficient

Fig. 5.7 shows sheet scattering coefficient of untreated and treated recycled pulps as a function of number of cycles. The figure also shows the trend lines for untreated pulps during recycling. Alkali treatment causes increase in scattering coefficient for both bagasse and wheat straw recycled pulps; the rise for wheat straw is more than the bagasse. As expected, refining of alkali treated pulps in PFI mill decreases scattering coefficient, and thereby increases the fiber bonding. On refining to the same number of revolutions in PFI mill, the reduction in scattering coefficient of wheat straw recycled pulps is much more than the reduction in bagasse recycled pulps. The scattering coefficient of recycled wheat straw pulp after refining was found to fall even below that of the virgin pulp. After refining of bagasse recycled pulps, the scattering coefficient remained greater than that of the virgin pulp. This suggests that the recovery of fiber bonding by refining of recycled pulp is greater for wheat straw than bagasse.

The scattering coefficient for R48 fraction was found to be nearly same as that for R100 fraction in the recycled pulps (Table- A3.3, page 143) agreeing with

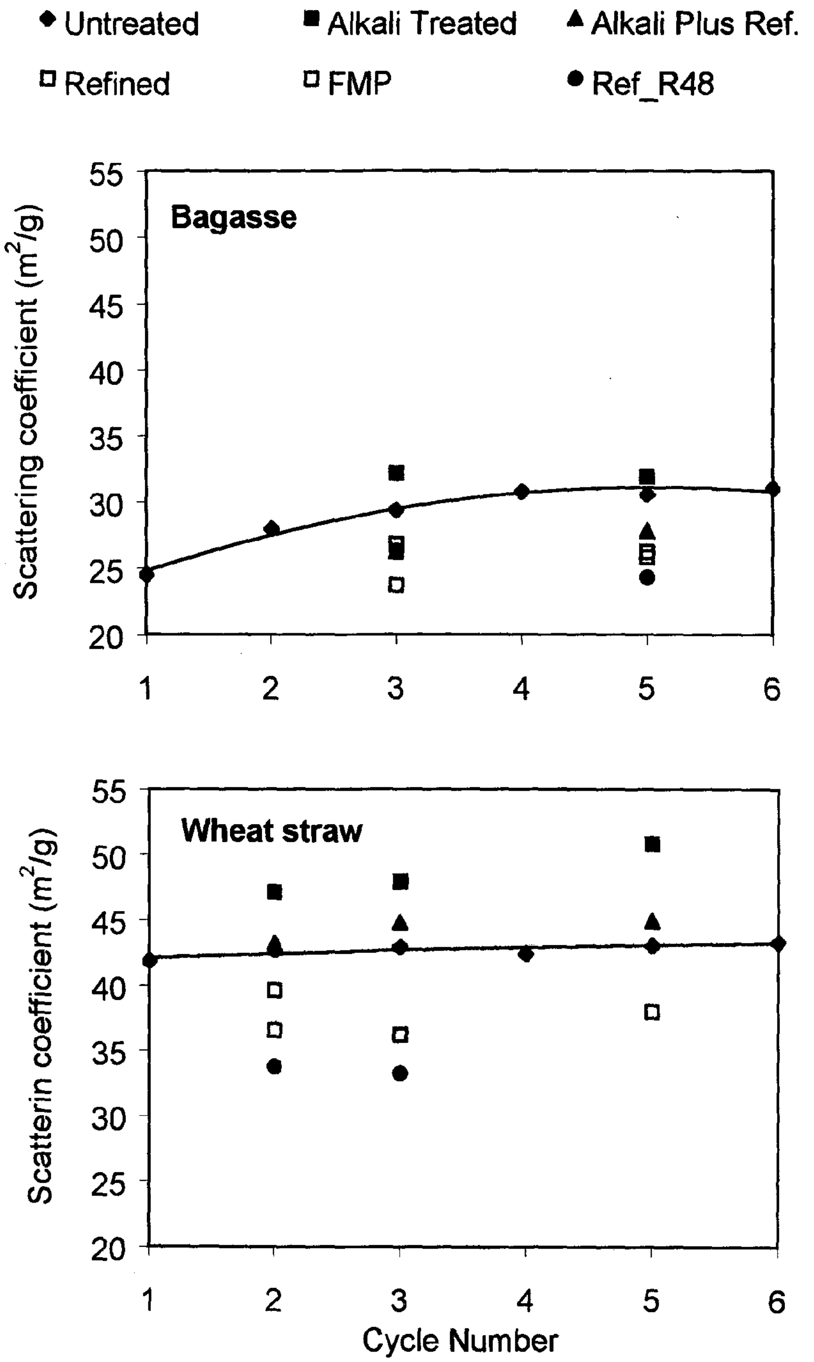


Fig. 5.4: Effect on scattering coefficient of various treatments on recycled pulps.

the earlier observations that the light-scattering coefficient of a sheet is independent of fiber length (153).

5.3.2 EFFECT ON STRENGTH PROPERTIES

Tensile Index

Fig. 5.5 shows the effect of various treatments on tensile index for recycled pulps of bagasse and wheat straw. Both the pulps were beaten in a Valley beater in their virgin stage to nearly same freeness. Initial tensile strength of the bagasse pulp was about two times the strength of the wheat straw pulp. On recycling, the loss in tensile index for bagasse pulp was significant, but the loss in strength of wheat straw pulp was marginal. Alkali treatment alone did not have much effect on the tensile strength of these pulps at different cycles. Refining with and without alkali treatment resulted in increase in tensile strength of both the pulps. The tensile strength of recycled wheat straw pulp after these treatments was even higher than the strength of the virgin pulp. But this improvement in tensile index could be achieved with a significant increase in slowness of the pulps. Fig. 5.6 shows variations in tensile index with freeness of untreated and treated recycled pulps, and their different fractions of bagasse and wheat straw.

Recycling has little effect on tensile strength of R48 fractions of these pulps (Table- A3.4, page 144). It is interesting to note that short fibers of recycled bagasse pulps have higher tensile index than long fibers. For wheat straw pulps, the long fiber fraction has greater tensile strength than fines fraction. Data (Tables A3.2 & A3.4, page 142,144) show that coarser fraction of bagasse recycled pulp have low strength at low sheet density than that of coarser fraction of wheat straw recycled pulp.

Refined long fibers (R48) of recycled pulps of the two raw materials show almost same tensile index, as shown in Fig. 5.5. This shows that this fiber fraction

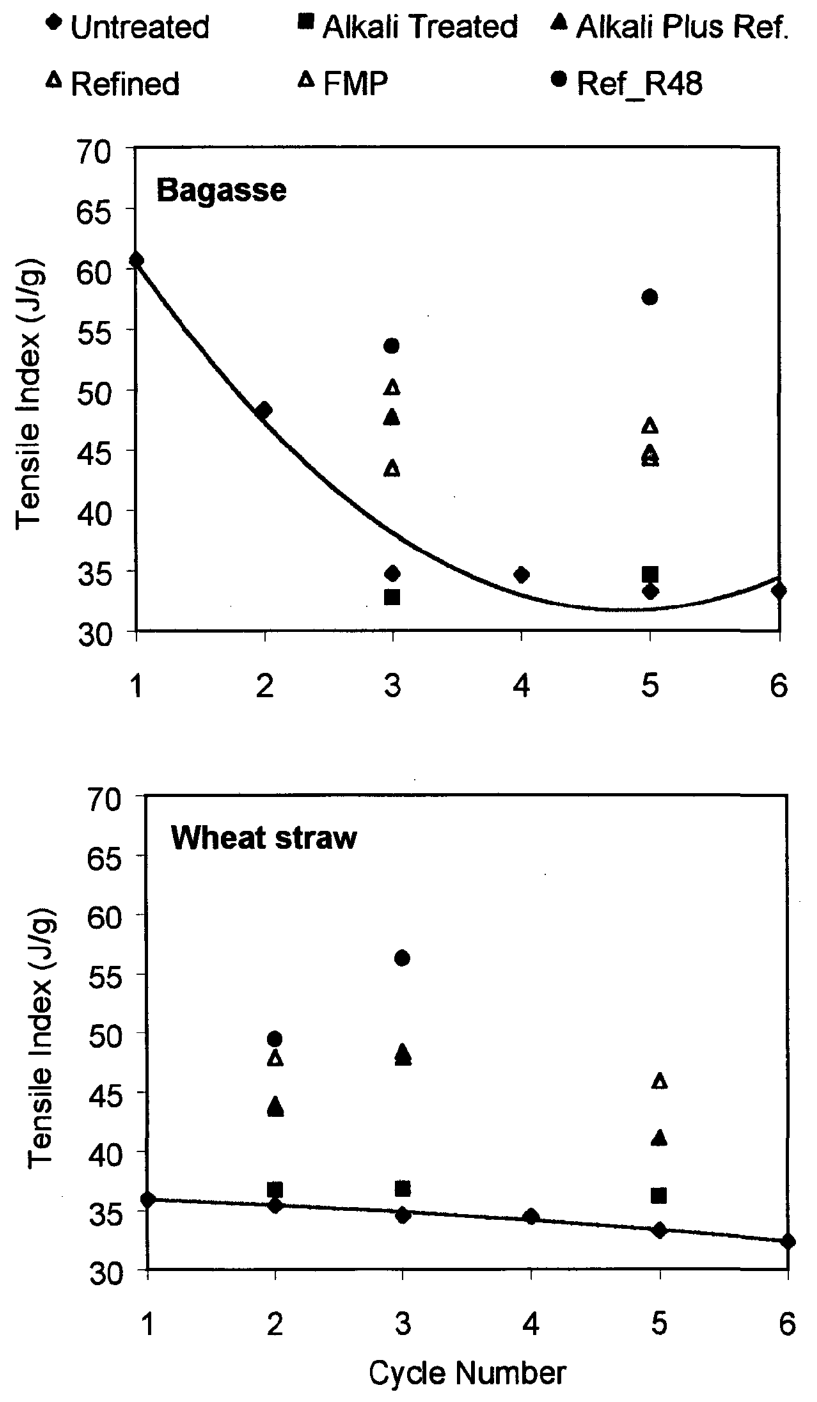


Fig. 5.5: Effect on tensile Index of the various treatments on recycled pulps.

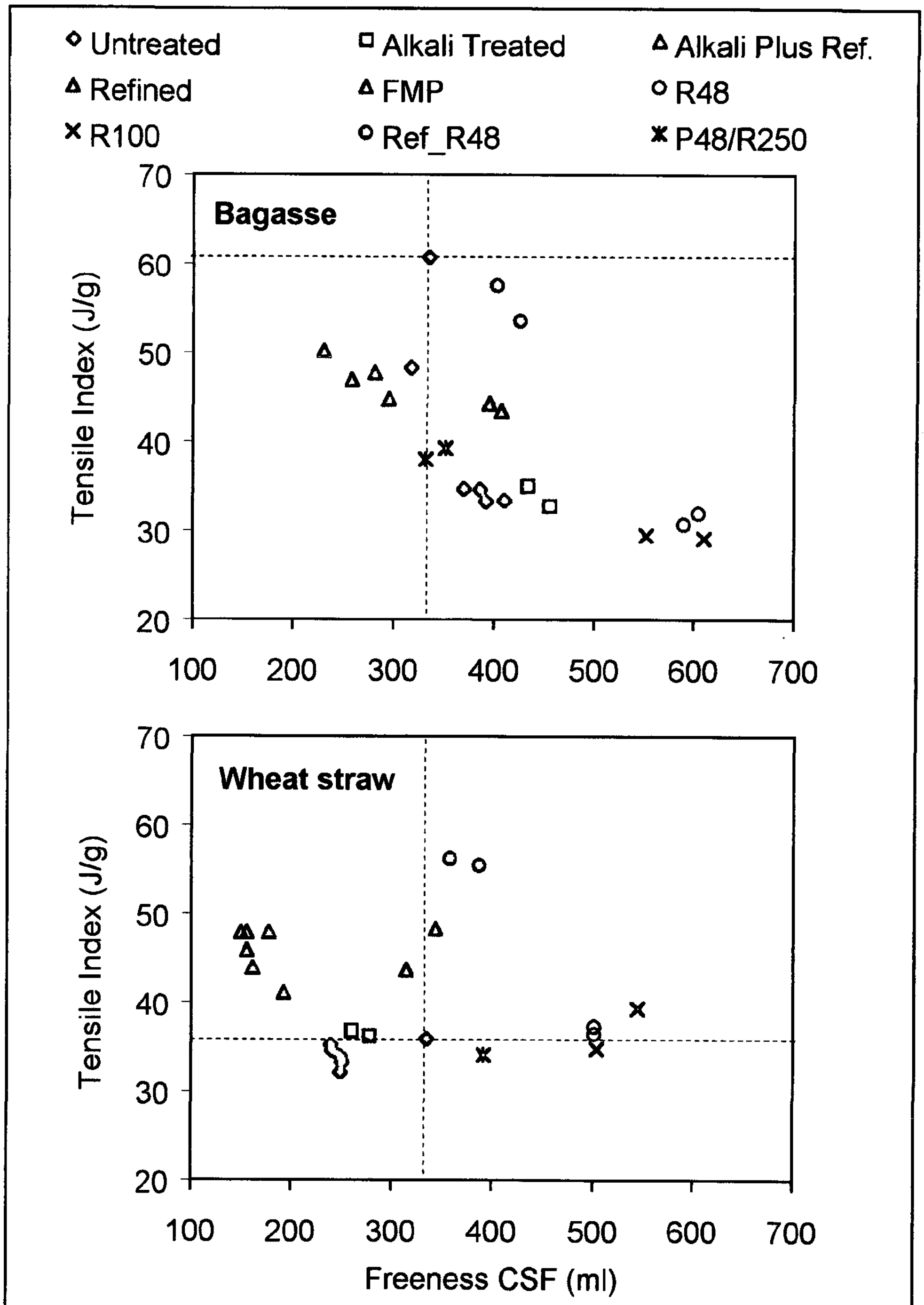


Fig. 5.6: Relationship between tensile index and freeness of recycled chemical pulps and their fractions treated by various methods. Dotted lines represent initial tensile index and freeness levels.

of recycled pulps of two raw materials after refining has same bonding potential for tensile failure. Mixture of refined R48 fraction with fines fraction in 1:1 ratio (fractionated mixed pulp) has the tensile index equal or slightly less than that of refined whole recycled pulp but at a much greater freeness. The increase in freeness is particularly significant for wheat straw pulp. (Fig. 5.6)

Tear Index

Fig. 5.9 shows the effect of various treatments on tear strength as a function of sheet density of recycled pulps. Recycling has a greater effect on the tear strength of bagasse pulp than the wheat straw pulp (Chapter 4, page 80).

All the treatment methods studied enhanced the tear index of recycled bagasse pulp. The effect on wheat straw pulp was small. Alkali treatment on bagasse recycled pulps increases tear index at same sheet density. Refining without or with alkali treatment increases both tear index and sheet density above the initial level. For wheat straw recycled pulps tear index remains almost constant for wide range of sheet densities on various treatments (Fig. 5.7).

Coarser fractions, R48 and R100, of recycled pulps have higher tear index at low sheet density than the whole pulp; tear index increases with fiber length (38). These fractions of recycled pulps of wheat straw have high tear index and sheet density than the fractions of recycled pulps of bagasse. Refining of R48 fraction of recycled pulp of bagasse increases both tear index and sheet density. Refining of R48 fraction of wheat straw recycled pulp increase the sheet density at nearly constant tear index. Interestingly, refined R48 fractions of recycled pulps of both bagasse and wheat straw have nearly the same tear index as they have nearly equal tensile and burst strengths.

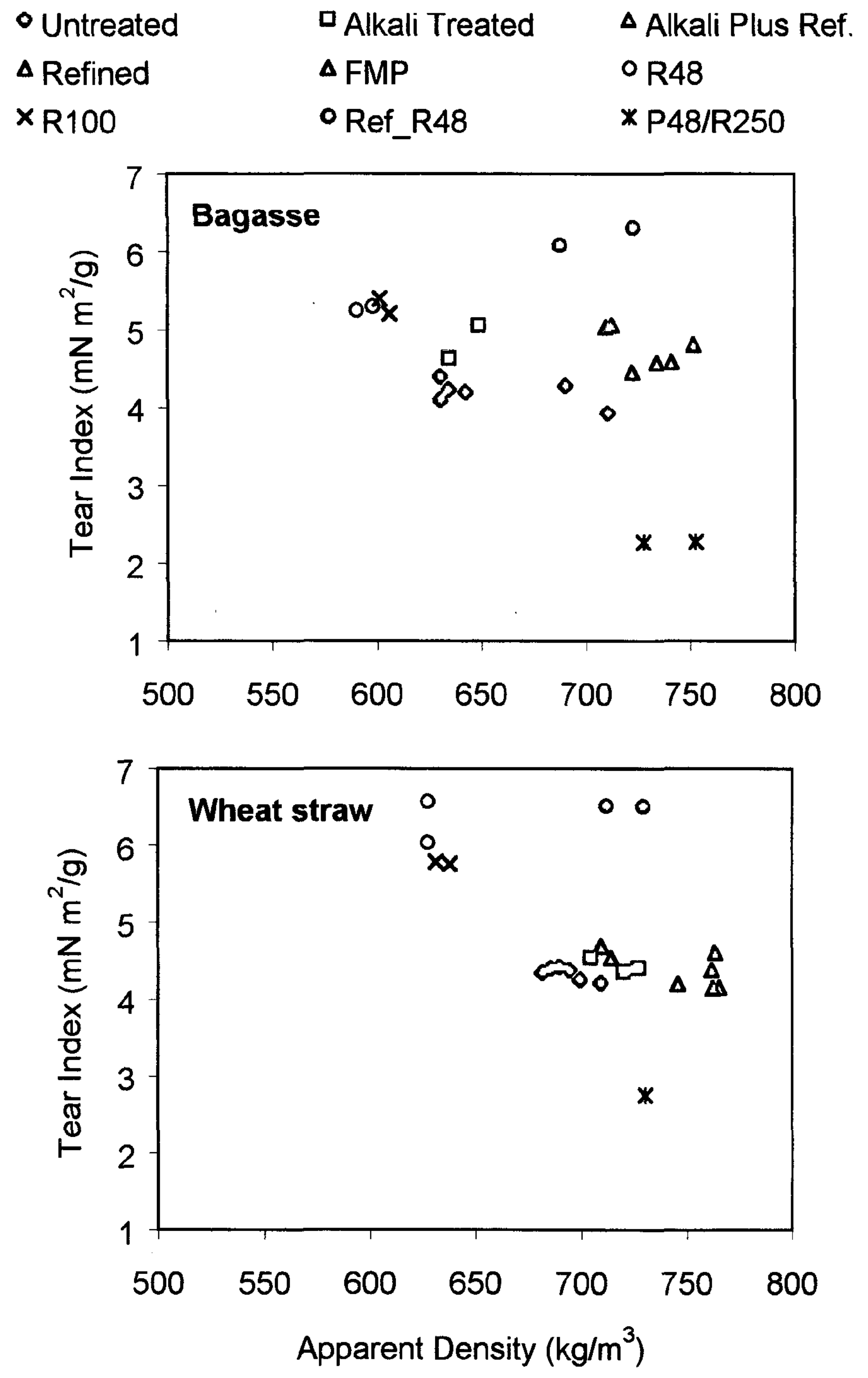


Fig. 5.7: Relationship between tear index and apparent density of recycled chemical pulps and their fractions treated by various methods.

Fractionate mixed pulps of bagasse recycled pulps have nearly same tear index and sheet density as that of the refined whole pulp but at higher pulp freeness. Fractionate mixed pulps of wheat straw recycled pulps also show similar behaviour but at slightly lower sheet density than refined whole pulp.

Folding Endurance

Table 5.4 shows the effect of various treatments on folding endurance of recycled pulps of bagasse and wheat straw. All the treatments increase the folding endurance of the recycled pulps. In general, the effect on folding endurance is similar to the effect on tensile and burst strength. However, refining or alkali treatment of recycled pulps resulted in a relatively higher improvement in folding endurance than the improvement in tensile strength. It is believed that folding endurance is a measure of the strength and flexibility of paper (151). It appears, from the results of this study, that refining or alkali treatment of recycled pulp increases the fiber flexibility to a greater extent than it increases the fiber bonding.

5.3.4 TENSILE INDEX – SCATTERING COEFFICIENT RELATIONSHIP

Fig. 5.13 shows the tensile index plotted as a function of scattering coefficient. Values on this plot correspond to samples of untreated and treated whole pulps and their fractions at different cycles for a given type of pulp. It is interesting to note that all the data points lay on a straight line for bagasse as well wheat straw pulps. This appears that the tensile index – scattering coefficient (T-S) relationship is unaffected by the recycling or refining of the pulp. This is in agreement with the findings of Ingmanson and Thode (154) that the T-S relationship was independent of degree of beating. Another interesting observation is that for wheat straw pulp, the alkali treatment with or without refining tends to increase the scattering coefficient above the T-S line.

Table- 5.4: Effect on folding endurance of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56)		Wheat straw (WCP49)	
		Fold End.	% Ch.	Fold End.	% Ch.
Initial value	1	1.03		0.96	
Untreated	2	1.10		0.90	
	3	0.90		0.87	
	5	0.76		0.89	
Alkali treated	2			1.01	12.22
	3	0.90	0.00	1.02	17.24
	5	0.97	27.63	1.00	12.36
Refined	2			1.26	40.00
	3	1.49	65.56	1.25	43.68
	5	1.45	90.79	1.18	32.58
Alkali treated plus Refined	2			1.31	45.56
	3	1.29	43.33	1.41	62.07
	5	1.36	78.95	1.17	31.46
R48 Fraction	2	0.98		1.14	
	3	0.78		1.11	
	5	0.75		1.29	
R100 Fraction	2	0.86		1.10	
	3	0.75			
	5	0.72		1.15	
Fines Fraction P48/R250	2			0.70	-22.22
	3	0.48	-46.67		
	5	0.30	-60.53		
Refined R48 Fraction	2			1.63	42.98
	3	1.83	134.62	1.73	55.86
	5	1.76	134.67		
Fractionated Mixed Pulp (FMP)	2			1.25	38.89
	3	1.09	21.11	1.16	33.33
	5	1.20	57.89		

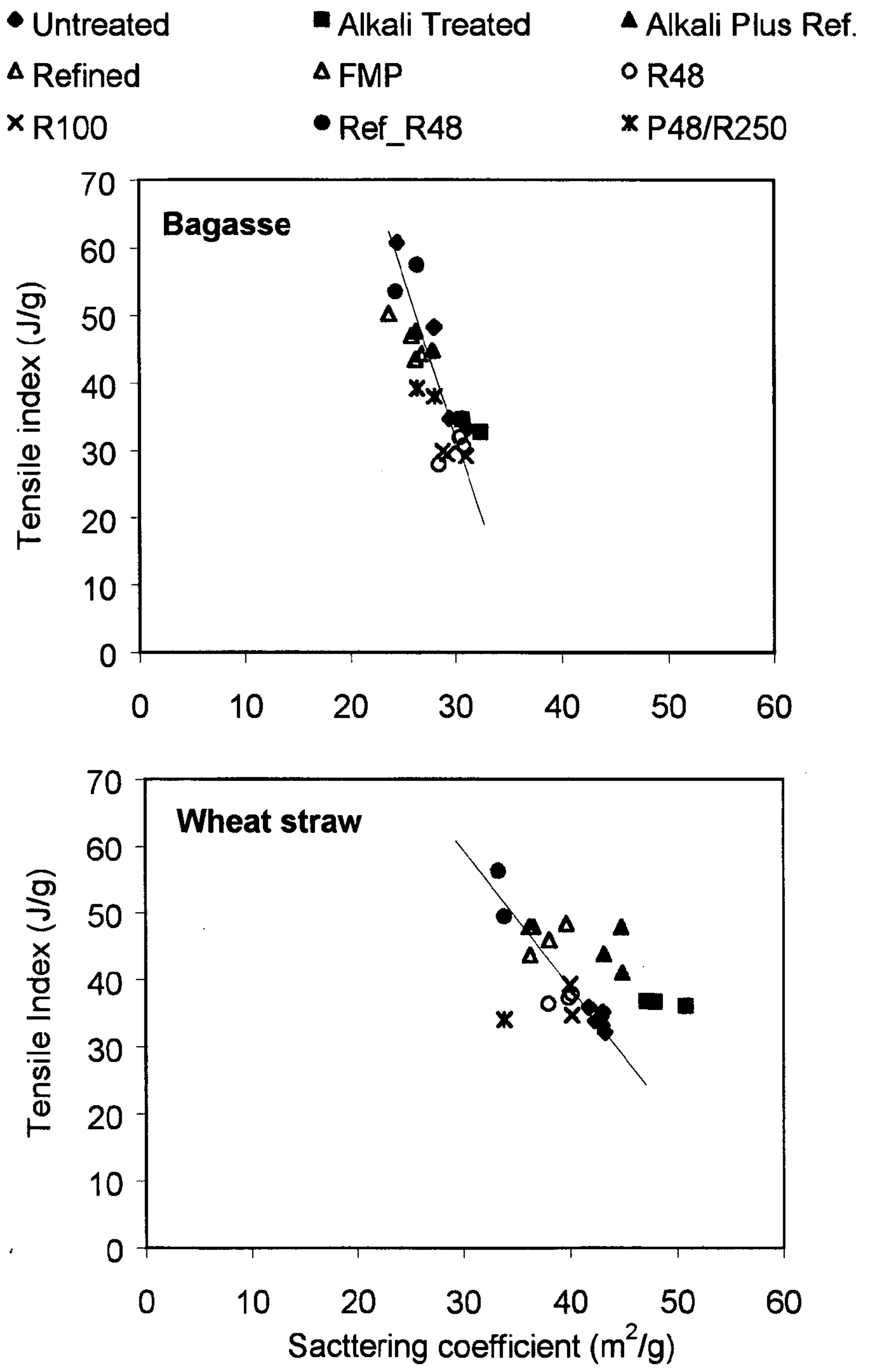


Fig. 5.8: Relationship between tensile index and scattering coefficient of recycled chemical pulps and their fractions treated by various methods.

5.3.3 ZERO-SPAN TENSILE INDEX

Fig. 5.8 shows effect of different treatments on zero-span tensile index (ZSTI) of recycled bagasse and wheat straw pulps. The plots are quite similar to the tensile index plots (Fig. 5.5) except that the ZSTI values are much larger than the tensile index values. Most of the observations made about the effect on tensile strength are true with ZSTI. To summarize; the alkali treatment alone does not have much effect on the ZSTI of these pulps at different cycles; refining without or with alkali treatment have resulted increase in ZSTI of both the pulps; the ZSTI of recycled wheat straw pulp after these treatments is even higher than the ZSTI of the virgin pulp.

Recycling has little effect on ZSTI of R48 fractions of these pulps (Table A3.7). The long fiber fraction has greater ZSTI than fines fraction for both pulps. Refined long fibers (R48) of recycled pulps of the two raw materials show almost same ZSTI, as given in Table A3.7 (page 147).

The ZSTI was measured to study the effect of recycling and the methods of fiber treatment on the intrinsic strength of the fibers. The other measure that is usually associated with the fiber strength is the pulp viscosity. The pulp viscosity is related with the degradation of cellulose. Since, in the pulp recycling process, mainly the physical changes in the fiber are taking place, the ZSTI was preferred over the viscosity. Seth and Chan (149) have shown that pulp viscosity is a poor predictor of fiber strength. Normal tensile testing indicates the combined effect of the strength of the fibers, their bonding, and variation in the paper structure. The zero-span tensile test provides a possibility to measure the fiber strength separated from other effects.

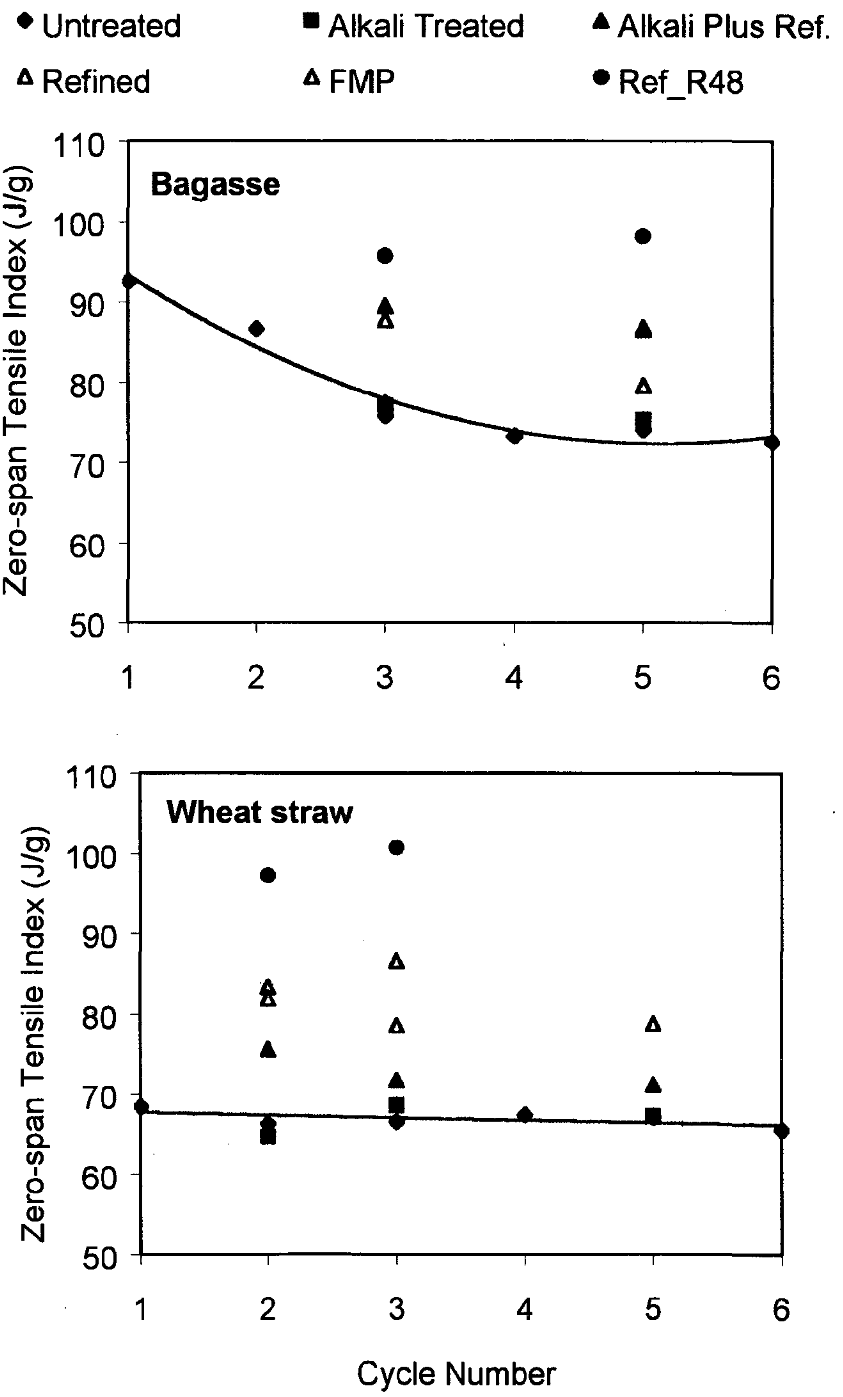


Fig. 5.9: Effect on zero-span tensile index of various treatments on recycled pulps.

While the above is generally considered true, many studies (148,149,155,157) point out that ZSTI is a complex function of fiber properties and process variables. Cowan (155) recommended use of rewetted sheets to eliminate the effect of fiber bonding. Gurnagul et al. (156) countered the suggestion by pointing out that rewetting of fibers reduced the strength of individual fibers, and therefore, wet ZSTS measurements did not have use as an index for dry fiber strength.

Zero-span tensile strength is dependent on crimps and kinks in the fiber (148,149). Mohlin & Alfredsson (148) have shown that the wet ZSTI increases with the beating of the fiber; increasing considerably with PFI mill refining but changing only slightly in an industrial refiner. Seth and Chan (149) found the similar relationships between the dry sheet ZSTS and the pulp freeness. They suggested that the ZSTI of pulp handsheets is a reliable index of fiber strength, provided the fibers are straight. As the pulp fibers are seldom straight and free from crimps and kinks, the ZSTS of these pulps is not true measure of fiber strength. A device such as a PFI mill, which beats the fibers gently and swells them, helps to straighten the fibers. The observed increase in ZSTI of recycled bagasse and wheat straw pulps is perhaps due to straightening of fibers on refining in PFI mill.

5.4 RELATIVE BONDED AREA (RBA)

Tensile strength of a fibrous network, such as paper, depends to a great extent on the strength of fiber-fiber bonds. An important parameter for accounting of bonding between fibers in a sheet of paper is relative bonded area (RBA). By definition, the RBA is the ratio of bonded surface to total surface area of the fibers. RBA depends on the cross-sectional dimensions and flexibility of fiber, wet pressing, and drying conditions of the sheet. RBA is commonly estimated from the specific scattering coefficient of the sheet as (154):

$$\mathrm{RBA}=\frac{S_o-S}{S_o} \qquad (5.1)$$

Where S_o is the scattering coefficient of completely unbonded fibers and S is scattering coefficient of a paper sheet.

For estimation of S_o, handsheets of bagasse and wheat straw pulps were prepared at varying degree of wet pressing (1 kN/m^2 to 8 kN/m^2) from the unbeaten freely air-dried pulps and from the pulp pads stored after four cycles. The handsheets were tested for tensile index and scattering coefficient (Table- A3.8, page 149). Fig. 5.10 shows relationships between scattering coefficient and tensile strength for different pulps. The data points for the recycled and refined recycled pulps have also been included. The curves were extrapolated to zero tensile index to give the value of S_o, and relative bonded area was calculated using Eq. 5.1.

5.4.1 EFFECT OF RECYCLING OF PULPS ON RBA

Fig. 5.11 shows the decrease in RBA on recycling of bagasse and wheat straw pulps. Fig. 5.12 shows that tensile index is linearly related with RBA for these pulps. However, even for the same raw material, tensile index – RBA relationship depends on the type of pulping process. The two chemical pulps of wheat straw have a large difference in tensile index for the same RBA values.

5.4.2 EFFECT OF REFINING OF RECYCLED PULPS ON RBA

Fig. 5.13 shows the change in RBA during recycling of BCP56 and WCP49 and for change in RBA when refining is employed to enhance the strength of the recycled whole pulps and their fractions. The curves are quite similar to the curves obtained for tensile index and zero-span tensile index (Fig. 5.5 and 5.9, page 101,109).

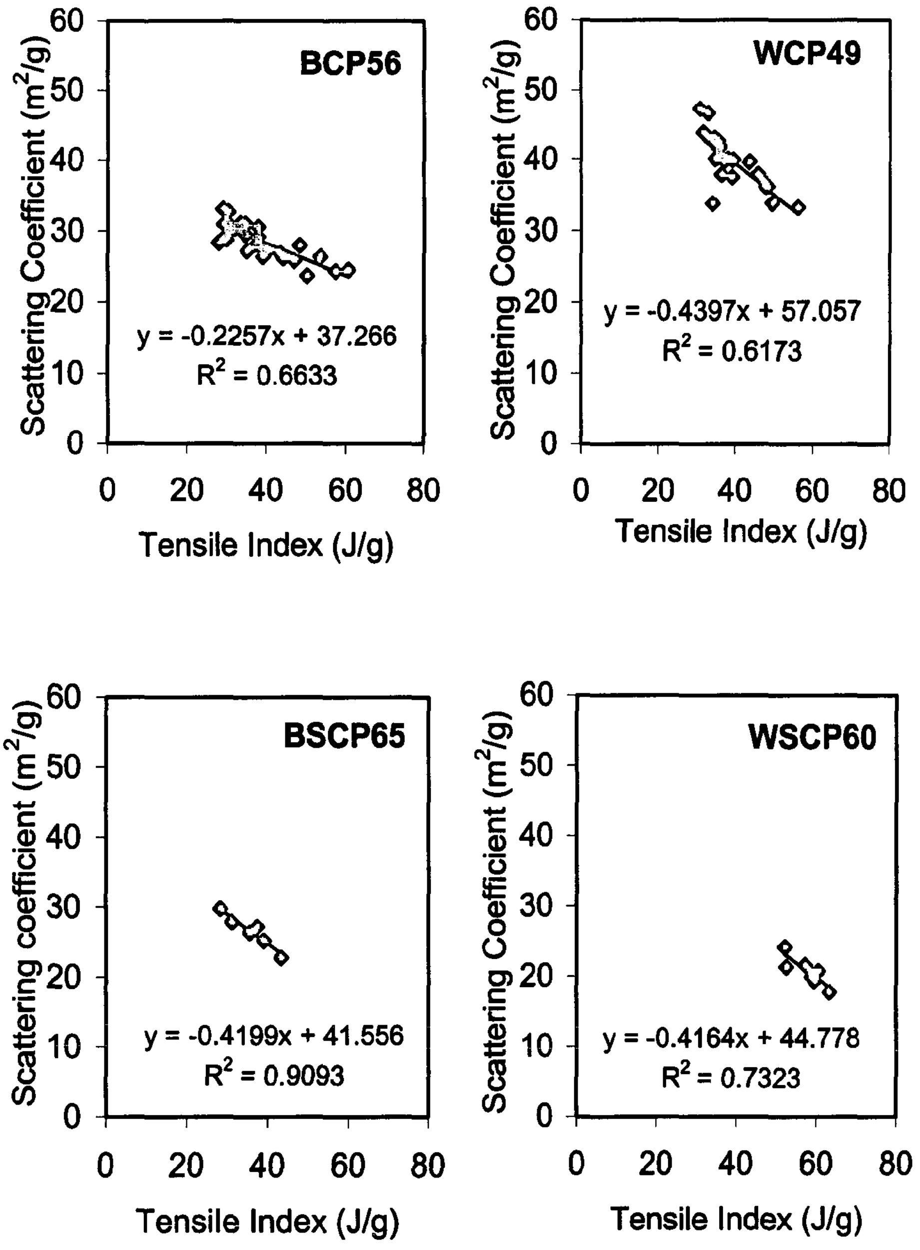


Fig. 5.10: Determination of scattering coefficient of unbonded fibers from scattering coefficient versus tensile index relationship.

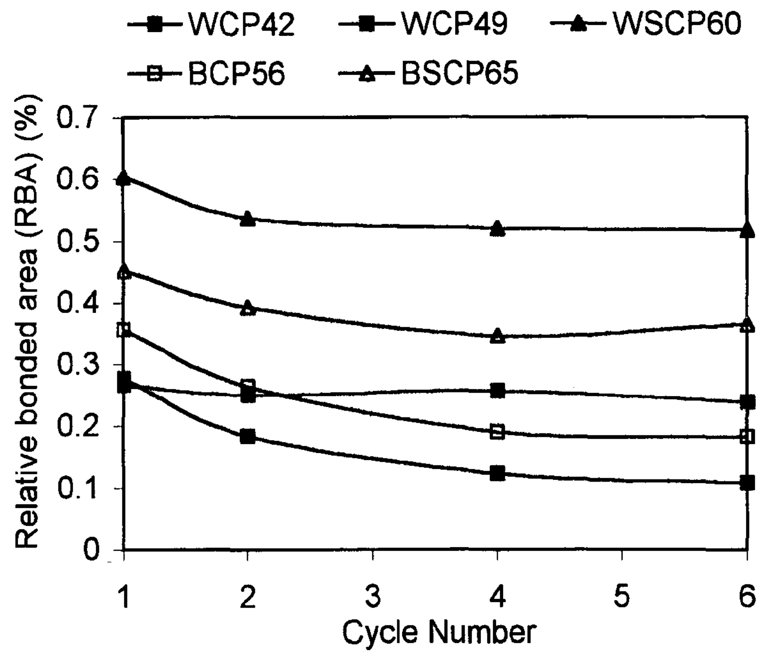


Fig. 5.11: Effect of recycling on relative bonded area (RBA) of pulps.

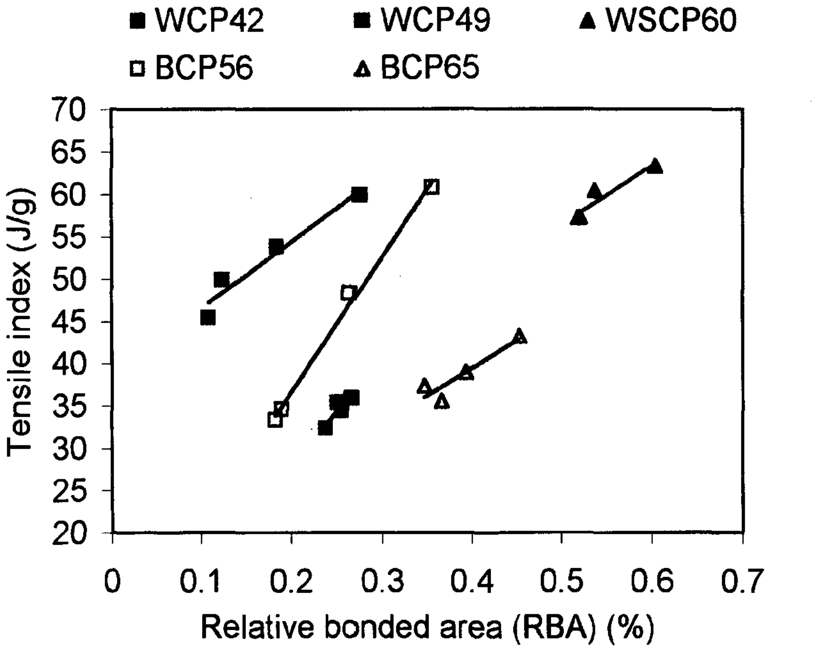


Fig. 5.12: Relationship between tensile index and relative bonded area of recycled pulps.

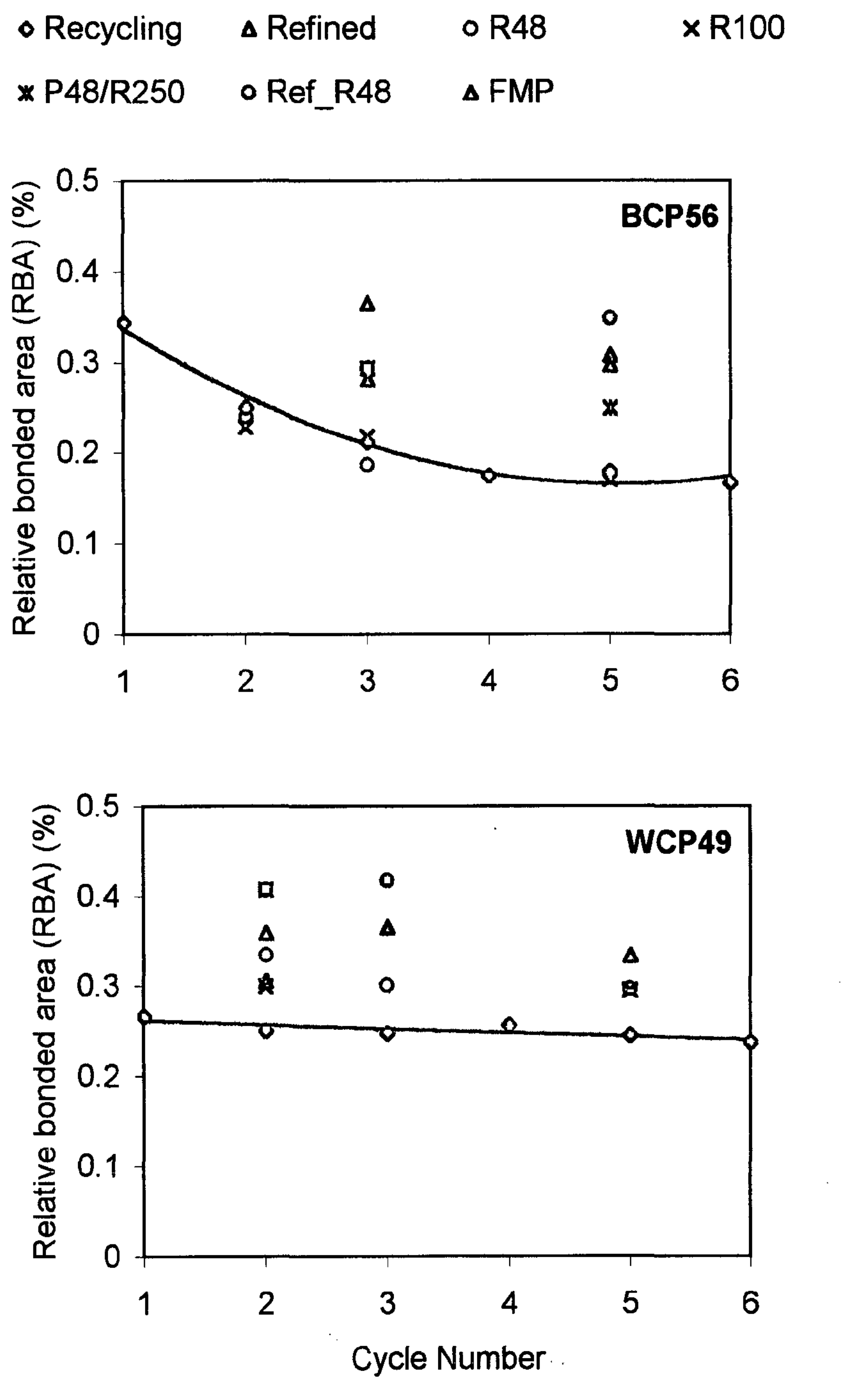


Fig. 5.13: Effect on RBA of refining of recycled chemical pulps and their fractions.

5.5 FINDINGS

1. Freeness of the recycled pulps decreases sharply on refining, but the drop in freeness is less when the refining is carried out after treating the pulps with alkali. The freeness increases slightly when the recycled pulps are treated with alkali alone. Reduction in freeness due to refining is more severe for wheat straw pulps than for bagasse pulps.
2. Very fine particles (P250) contribute to a great deal in the slowness of the wheat straw pulp, as indicated by a significant rise in freeness when this fraction was removed from the pulp.
3. A mixed pulp of refined coarse fraction (R48) and unrefined fines fraction (P48/R250) of the recycled pulps of bagasse and wheat straw could be prepared to have much higher freeness for equivalent strength values.
4. None of the treatments used in this study could raise the swellability (WRV) of recycled pulps to the levels of virgin pulps.
5. The WRV of the coarse fraction (R48) of the recycled pulps is less than the WRV of the fines fraction (P48/R250).
6. Roughness of the sheet was not appreciably affected by the treatments studied on the chemical recycled pulps of bagasse and wheat straw. Roughness of handsheets made from bagasse recycled pulp remains greater than the roughness of handsheets made from wheat straw pulp for both coarse and fine fractions.
7. Alkali treatment causes increase in scattering coefficient for both bagasse and wheat straw recycled pulps. Wheat straw pulps show a higher rise.
8. The tensile strength of recycled pulps was not affected much by alkali treatment alone.

9. The tensile strength was enhanced by refining, but with a significant reduction in freeness.
10. Mixture of refined coarse fraction (R48) with unrefined fines fraction (P48/R250) in 1:1 ratio had the tensile index nearly equal to that of refined whole recycled pulp but at a much greater freeness. The increase in freeness is particularly significant for wheat straw pulp.
11. A nearly common tensile index – scattering coefficient (T-S) relationship is observed for pulps recycled to different number of cycles, for their coarse and fines fractions, for refined whole pulps, refined coarse fractions, and mixtures of refined coarse fraction and unrefined fines fractions.
12. The tear strength of recycled bagasse pulp responded favourably to all the treatment methods studied. The effect of treatments on the tear strength of recycled wheat straw pulp was small. The observation that both the tear strength and tensile strength responded favourably to refining and other treatment methods points towards a different nature of agricultural residue pulps from softwood pulps.
13. Tear index of the mixture of refined R48 fraction and the fines fraction was at about the same level as of the refined whole pulp but at higher pulp freeness.
14. The folding endurance of the recycled pulps increased as a result of all the methods of treatment studied. The increase due to refining with or without alkali treatment was well passed the folding endurance of the virgin pulps.
15. The zero-span tensile strength (ZSTS) of the recycled pulps responded in a manner quite similar to the tensile strength.
16. The observed increase in ZSTS of recycled bagasse and wheat straw pulps could perhaps be due to straightening of fibers in PFI mill.

17. Relative bonded area decreases with recycling for bagasse chemical pulp but remains unchanged for wheat straw chemical pulp. The value of RBA increases with refining of the recycled pulps.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

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CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The most significant effect of recycling of pulp is the loss in its tensile strength. Therefore, the recycling potential of pulps, in most studies, has been judged in terms of tensile strength. The main conclusions of the present study are as under:

1. Recycling potential of a pulp is dependent on the type of raw material, pulping method, pulp yield, and its initial freeness.
2. Wheat straw pulps have higher recycling potential than bagasse pulps. For both bagasse and wheat straw, the low yield chemical pulps suffer greater loss in tensile strength than the higher yield pulps.
3. The loss in tensile strength of bagasse chemical pulp is of the order of the loss reported for softwood and hardwood pulps.
4. During the process of recycling, the loss of fines (P200) of bagasse pulps is considerably higher than the loss of fines of wheat straw pulps. Therefore, on recycling, the freeness of wheat straw pulps decreases considerably. The high recycling potential of wheat straw pulps is, perhaps, due to the high retention of fines in these pulps during recycling.
5. The proportions of alpha, beta, and gamma cellulose do not change with recycling for both bagasse and wheat straw chemical pulps. However, the initial gamma cellulose content in a pulp seems to affect its recycling potential. The bagasse pulp, due to lower gamma cellulose content, suffered a greater loss in strength than wheat straw pulp on recycling.
6. Water retention value (WRV) of bagasse and wheat straw pulps decrease gradually with recycling. This behaviour of nonwood pulps is unlike wood pulps where the major loss in fiber swelling occurs in the first cycle.

7. Zero-span tensile strength (ZSTS) decreases with recycling for both bagasse and wheat straw pulps. The loss in ZSTS for bagasse pulps is greater than the loss for wheat straw pulps. The lower the yield of pulp the greater is the loss in ZSTS. The loss in ZSTS on recycling may be due to increase in fiber curling rather than loss in intrinsic fiber strength.
8. Refining of recycled pulps increases the tensile strength to a large extent but with a sharp decrease in freeness. Refining of alkali treated pulps causes a lower decrease in freeness.
9. Reduction in freeness due to refining is more severe for wheat straw recycled pulps than for bagasse recycled pulps.
10. A mixed pulp of refined coarse fraction (R48) and unrefined fines fraction (P48/R250) of the recycled pulps can be prepared to have much higher freeness than the refined whole pulp for equivalent strength values. This is particularly significant for wheat straw pulps where the reduction in freeness on refining is very high.
11. Refining of recycled pulps increases zero-span tensile strength (ZSTS) in a manner quite similar to the tensile strength. The increase in ZSTS on refining is relatively more significant for the coarser (R48) fraction. The observed increase in ZSTS may be due to straightening of fibers as the refining was carried out in a PFI mill.

6.2 RECOMMENDATIONS

Important conclusions derived from the analysis of the experimental data have been presented in the previous section. At the time of analyzing data, some shortcomings in the planning of the experiments were noticed. It is desired that some of the conclusions drawn from the study be supported further by experimental evidence. It is recommended that the following points may be considered in a future study of this type.

1. Experiments should be planned such that the relationships between the recycling potential of a pulp and its fundamental characteristics such as intrinsic strength, morphological and bonding characteristics of fiber are established in the light of existing theories. Effect of recycling on the relative bonded area and bond shear strength should be studied.
2. Long fibers and other finer fractions of the recycled pulps should be compared with the corresponding fractions in their virgin state to see whether the recycling affects these fractions differently.
3. The role of fines (P200) fraction on strength properties of pulp in the virgin and recycled state should be evaluated. There is some evidence that the fines of wheat straw pulp appear to behave differently from the fines of wood pulp.
4. The effect of recycling on inter-fiber bonding of different fractions of pulp should be studied in greater details using newer techniques such as transmission electron microscopy (TEM).

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Appendix – 1

STANDARDIZATION OF CONDITIONS FOR WRV DETERMINATION

To standardize the conditions we used a laboratory prepared unbleached eucalyptus kraft pulp and centrifuged it at different force and time conditions. In our laboratory we are having a centrifuge meant for the same purpose, which is having a maximum capacity to generate a centrifugal force of 6500 g. The results obtained are given in Table- A1.1.

In the selected eight conditions, the results leads to the conclusion that the pulp centrifuged at 300Ogf for 15 to 30 min gives the most stable values for WRV. These results are also in match with the findings of Jayme (10) and, Scallan and Carles (55).

Table- A1.1: WRV for unbleached eucalyptus kraft pulp at eight different centrifuging conditions.

S.No.	Centrifugal Force (N)	Time of centrifugation (min)	Average WRV (g/100g of pulp)	Standard Deviation
1	900	30	204.5	± 4.81
2	900	60	184.3	± 5.41
3	1500	30	182.1	± 3.89
4	1500	45	178.2	± 3.26
5	2000	30	177.3	± 4.38
6	3000	15	165.8	± 3.17
7	3000	30	162.5	± 3.13
8	3500	15	164.8	± 2.58

Appendix – 2

EXPERIMENTAL DATA ON RECYCLING OF PULPS

Table- A2.1: Methods used for testing of pulp properties.

Properties	
Bauer-McNett fiber classification	T233
Freeness of pulp (Canadian standard method)	T 227
Drainage time of pulp	T 221
Air resistance of paper	T460
PS Porosity (ml/min)	Ref. 143
Roughness of paper and paperboard (Print-surf method)	T 555
Zero-span breaking strength of pulp (dry zero-span tensile)	T 231
Tensile breaking properties of paper and paperboard	T 494
Bursting strength of paper	T 403
Internal tearing resistance of paper (Elmendorf- type method)	T 414
Fold Endurance	SCAN-P 17:77
R_∞ (%) FMY/C	Ref. 144,145
R_o (%) FMY/C	Ref. 144,145
Scattering and Absorption Coefficient (m^2/kg)	Ref. 144,145
Alpha, beta and gamma cellulose of the pulp	T203

Table- A2.2: The effect on pulps drainage characteristics during recycling.

Pulp Type	Cycle No.	CSF (ml)	WRV (g/100g of pulp)	Drainage Time (s)
BCP56	1	335	203.04	7.75
	2	317	170.32	9
	4	386	137.9	9
	6	410	130.61	9
WCP42	1	349	220.8	8
	2	279	185.7	10
	4	275	157.1	10.5
	6	280	148.11	10
WCP49	1	334	177.33	9
	2	239	166.33	11.75
	4	248	163.76	12
	6	248	149.36	12
BSCP65	1	289	210.92	-
	2	260	189.87	-
	4	238	155.84	-
	6	241	150.8	-
WSCP60	1	306	259.17	10
	2	260	214.75	10.5
	4	255	186.7	10.5
	6	241	179.54	10.5
BCMP	1	224	162.89	-
	2	257	161.22	-
	4	359	153.68	-
	6	372	155.38	-

Table A2.3: The effect of recycling on BCP56.

Properties	**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (g/cm^3)	695.41 (5.58)	640.96(4.67)	630 (2.93)	630 (5.14)
Air Resis. (Gurley) (Sec.)	129.31(8.84)	70.5(15.05)	26.13(5.58)	17.5 (4.78)
PS Porosity (ml/min)	103.25	210.63	649.6	OOR
Roughness 5 Kgf/cm^2	5.1	5.78	>6	>6
(µm) 20 Kgf/cm^2	4.09	4.42	4.78	4.85
Zero-span Ten. Index (J/g)	92.54(2.18)	86.66 (5.6)	73.33(9.14)	72.58(3.04)
Tensile Index (J/g)	60.74(6.39)	48.34(2.55)	34.65(2.77)	33.39(11.21)
Burst Index (kPam^2/g)	3.65 (5.33)	2.96 (3.5)	1.79 (9.8)	1.4 (9.26)
Tear Index (mNm^2/g)	3.93(2.76)	4.28(2.69)	4.4 (1.45)	4.1 (3.36)
Fold Endurance	1.03 (28.92)	1.1 (9.89)	0.87 (11.2)	0.72 (9.88)
R_∞ (%) FMY/C	77.84(0.75)	80.23 (0.25)	80.84 (0.3)	80.8 (0.17)
Scat. Coeff. (m^2/kg)	24.49	27.97	30.81	31.08
Abs. Coeff. (m^2/kg)	0.77	0.68	0.70	0.71
Opacity (%)	75.68	77.96	80.23	79.33

Note: The values given in the table are the average values and the value in the brackets is the coefficient of variation for that property.

Table A2.4: The effect of recycling on WCP42.

Properties	**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (kg/m^3)	648.81 (5.7)	640.96 (4.04)	627.78 (4.25)	628.76 (4.29)
Air resistance (Gurley) (s)	144.31(14.4)	16.21(15.97)	8.67 (5.96)	13.3 (6.12)
PS Porosity (ml/min)	91	OOR	OOR	OOR
Roughness 5 Kgf/cm^2	4.5	5.5	5.54	5.8
(μm) 20 Kgf/cm^2	4.19	4.42	4.86	5.01
Zero-span Ten. Index (J/g)	83.2(2.18)	81.6 (5.6)	75.5 (9.14)	75.9 (3.04)
Tensile Index (J/g)	59.9 (6.39)	53.8 (2.55)	49.9 (2.77)	45.4 (11.21)
Burst Index (kPam^2/g)	3.27 (5.33)	2.8 (3.5)	2.71 (9.8)	2.61 (9.26)
Tear Index (mNm^2/g)	4.31(2.76)	4.71(2.69)	4.78 (1.45)	4.97 (3.36)
Fold Endurance	1.57 (10.69)	1.34 (8.6)	1.31 (5.14)	1.36 (9.19)
R_∞ (%) FMY/C	72.39 (1.34)	71.7 (0.15)	70.86 (0.26)	70.58 (1.61)
Scat. Coeff. (m^2/kg)	35.13	39.66	42.61	43.34
Abs. Coeff. (m^2/kg)	1.85	2.22	2.55	2.66
Opacity (%)	86.99	88.68	90.85	91.57

Note: The values given in the table are the average values and the value in the brackets is the coefficient of variation for that property.

Table A2.5: The effect of recycling on WCP49.

Properties	**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (Kg/m^3)	681.16(1.90)	708.93(2.12)	694.01(2.02)	689.27(1.19)
Air Resist. (Gurley) (s)	77(5.7)	68(6.32)	70(4.65)	55.67(8.94)
PS Porosity (ml/min)	166.33	179.33	169.33	235
Roughness 5 Kgf/cm^2	4.15	4.3	4.77	4.72
(µm) 20 Kgf/cm^2	3.81	3.42	3.59	3.59
Zero-span Ten. Index (J/g)	68.41(1.02)	66.33(2.63)	67.42(3.58)	65.56(1.32)
Tensile Index (J/g)	35.91(4.60)	35.23(3.15)	33.90(4.23)	32.15(5.34)
Burst Index (kPam^2/g)	2.16(10.80)	1.98(6.26)	2.08(5.68)	1.74(8.22)
Tear Index (mNm^2/g)	4.34(3.75)	4.10(3.15)	4.38(4.91))	4.42(2.24)
Fold Endurance	0.98(5.89)	0.91(9.00)	0.87(12.16)	0.87(10.21)
R_∞ (%) FMY/C	82	81	80	79
Scatt. Coeff. (m^2/kg)	41.75(0.91)	43.05(2.08)	42.36(0.85)	43.26(1.77)
Abs. Coefficient (m^2/Kg)	0.84(1.13)	1.14(1.85)	0.99(1.44)	1.25(2.28)
Opacity	75.68	77.96	80.23	79.33

Note: The values given in the table are the average values and the value in the brackets is the coefficient of variation for that property.

Table- A2.6: The effect of recycling on BSCP65.

Properties		**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (g/cm^3)		597.92(2.52)	604.57(2.96)	592.22(0.92)	565.22(2.14)
Air Resist. (Gurley) (Sec.)		195(9.52)	116(6.68)	107(11.21)	110(13.21)
PS Porosity (ml/min)		74.8	138.4	139	132.8
Roughness	5 Kgf/cm^2	>6	>6	>6	>6
(μm)	20 Kgf/cm^2	5.17	>6	>6	>6
Zero span Tensile Index (J/g)		79.95(3.40)	72.40(2.49)	71.60(3.21)	69.98(2.02)
Tensile Index (J/g)		43.46(0.83)	39.35(3.94)	37.40(1.17)	35.39(5.52)
Burst Index (kPa-m^2/g)		1.83(9.47)	1.52(6.51)	1.11(6.74)	1.39(7.63)
Tear Index (mN m^2/g)		4.21(3.27)	4.15(2.89)	4.13 (0. 50)	3.88 (2.89)
Fold Endurance		1.08(8.15)	0.85(13.29)	0.78(1.82)	0.82(4.28)
R_∞ (%) FMY/C		75	71	73	72
Scatt. Coeff. (m^2/kg)		22.76(1.12)	25.17(2.25)	27.20(1.39)	26.33(1.76)
Abs. Coefficient (m^2/Kg)		0.98(1.91)	1.49(3.33)	1.37(2.47)	1.49(1.23)
Opacity (%)		77.4	83.37	82.44	83.29

Note: The values given in the table are the average values and the value in the brackets is the coefficient of variation for that property.

Table-A2.7: The effect of recycling on WSCP60.

Properties	**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (kg/m3)	601.29(4.63)	599.1(2.37)	578.52(2.13)	587.6(1.93)
Air Resist. (Gurley) (Sec.)	720(5.32)	178(8.45)	121(7.98)	140(8.23)
PS Porosity (ml/min)	32.8	84.4	95.5	91
Roughness 5 Kgf/cm^2	5.3	>6	>6	>6
(μm) 20 Kgf/cm^2	4.39	5.01	5.28	5.28
Zero-span Ten. Index (J/g)	93.71(4.98)	90.12(2.33)	91.31(4.37)	90.29(2.39)
Tensile Index (J/g)	63.17(5.08)	60.07(4.12)	57.78(5.55)	56.45(5.76)
Burst Index (kPa m^2/g)	4.56(7.23))	4.12(14.93)	3.49(8.79)	4.17(5.89)
Tear Index (mNm^2/g)	3.85(3.83)	4.16(3.25)	4.14(2.26)	4.27(0.75)
Fold Endurance	1.79(10.52)	1.54(12.00)	1.37(16.73)	1.53(13.42)
R_∞ (%) FMY/C	73	74	72	71
Scat. Coeff. (m^2/kg)	17.64(4.48)	20.67(1.59)	21.56(1.44))	21.58(0.86)
Abs. Coeff. (m^2/kg)	0.91(2.42)	0.98(3.27)	1.15(1.94))	1.26(1.11)
Opacity (%)	76.71	75.68	77.78	78.87

Table-A2.8: The effect of recycling on BCMP

Properties	**I- cycle**	**II- cycle**	**IV- cycle**	**VI- cycle**
Apparent Density (kg/m^3)	355.56(3.63)	342.12(1.70)	382.21(2.95)	392.5(2.92)
Air Resist. (Gurley) (s)	4.5	4.75	5.5	5
Zero-span Ten. Index (J/g)	52.87(3.27)	55.42(3.86)	54.36(3.99)	53.21(3.96)
Tensile Index (J/g)	23.92(6.05)	24.24(3.86)	54.36(3.99)	53.21(3.96)
Burst Index (kPam^2/g)	0.73(10.92)	0.79(2.61)	0.73(9.58))	0.67(9.84)
Tear Index (mNm^2/g)	3.49(6.07)	3.51(3.37))	3.53(5.90)	3.36(6.77)
Double fold	4	5	5	4.5
R_∞ (%) FMY/C	59.0	57.0	55	54
Scatt. Coeff. (m^2/kg)	38.85(2.78)	37.06(2.49)	36.40(2.15)	36.43(3.73)
Abs. Coeff. (m^2/Kg)	5.58(2.76)	6.13(2.71)	6.56(3.24)	7.14(3.48)
Opacity (%)	96.56	96.03	96.03	96.95

Note: Note: The values given in the tables are the average values and the value in the brackets is the coefficient of variation for that property. Measurements for porosity and roughness on Print-surf tester cannot be done on the handsheets of BCMP because the values were out of the range of the apparatus.

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EXPERIMENTAL DATA ON REFINING OF RECYCLED PULPS

Table- A3.1: Effect on WRV of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56) WRV (g/100g of pulp)	Bagasse (BCP56) %Change	Wheat straw (WCP49) WRV (g/100g of pulp)	Wheat straw (WCP49) %Change
Initial value	1	203.04		177.33	
Untreated	2	170.32		165.34	
	3	152.44		162.86	
	5	135.32		150.02	
Alkali treated	2			166.96	0.98
	3	154.47	1.33	161.45	-0.87
	5	142.65	5.42	153.98	2.64
Refined	2			176.85	6.96
	3	162.79	6.79	167.75	3.00
	5	156.03	15.30	157.45	4.95
Alkali treated plus Refined	2			178.81	8.15
	3	171.33	12.39	169.69	4.19
	5	163.68	20.96	161.92	7.93
R48 Fraction	2	142.90		146.98	
	3			136.57	
	5	125.17		131.35	
R100 Fraction	2	146.89		141.63	
	3			138.77	
	5	126.57		131.1	
Fines Fraction P48/R250	2			182.96	10.66
	3	157.12	3.07		
	5	150.77	11.42		
Refined R48 Fraction	2			158.86	8.08
	3	154.23		155.22	13.66
	5	147.88	18.14		
Fractionated Mixed Pulp (FMP)	2			170.19	2.93
	3	161.57	5.99	167.93	3.11
	5	152.97	13.04		

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Table A3.2: Effect on apparent density of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56)		Wheat straw (WSCP49)	
		Density (Kg/m^3)	% Change	Density (Kg/m^3)	% Change
Initial value	1	695.41		681.16	
Untreated	2	640.96		700.64	
	3	642.23		699.13	
	5	634.12		685.32	
Alkali treated	2			726.79	3.73
	3	657.91	2.44	719.54	2.92
	5	648.53	2.27	703.95	2.72
Refined	2			793.59	13.27
	3	733.67	14.24	764.99	9.42
	5	709.24	11.85	745.48	8.78
Alkali treated plus Refined	2			762.12	8.77
	3	751.23	16.97	761.54	8.93
	5	712.20	12.31	763.15	11.36
R48 Fraction	2	597.78		627.13	
	3	589.90		627.22	
	5	599.42		631.70	
R100 Fraction	2	605.88		631.05	
	3	601.04			
	5	598.69		627.22	
Fines Fraction P48/R250	2			730.33	4.24
	3	727.50	4.61		
	5	752.34	8.19		
Refined R48 Fraction	2			711.65	13.48
	3	722	-98.78	729.16	16.25
	5	687.10	14.63		
Fractionated Mixed Pulp (FMP)	2			709.25	1.23
	3	740.69	15.33	713.72	2.09
	5	721.87	13.84		

Table- A3.3: Effect on scattering coefficient of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56) Scatt. Coeff. (m^2/Kg)	Bagasse (BCP56) % Change	Wheat straw (WSCP49) Scatt. Coeff. (m^2/Kg)	Wheat straw (WSCP49) % Change
Intial value	1	24.49		41.85	
Untreated	2	27.97		42.69	
	3	29.40		42.91	
	5	30.60		43.02	
Alkali treated	2			47.91	12.23
	3	32.19	9.49	47.09	9.74
	5	31.93	4.35	50.79	18.06
Refined	2			36.55	-14.38
	3	23.69	-19.42	36.15	-15.75
	5	25.83	-15.59	37.99	-11.69
Alkali treated plus Refined	2			43.17	1.12
	3	26.27	-10.65	44.78	4.36
	5	27.82	-9.08	44.89	4.35
R48 Fraction	2	28.36		37.93	
	3	30.33		39.84	
	5	30.71		40.11	
R100 Fraction	2	28.77		39.95	
	3	29.18			
	5	30.96		40.17	
Fines Fraction P48/R250	2			33.80	-20.82
	3	26.35	-10.37		
	5	27.99	-8.53		
Refined R48 Fraction	2			33.80	-10.89
	3	26.35	-13.12	33.24	-16.57
	5	24.31	-20.84		
Fractionated Mixed Pulp (FMP)	2			39.62	-7.19
	3	26.82	-8.78	36.22	-15.59
	5	26.22	-14.31		

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Table- A3.4: Effect on tensile index of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56)		Wheat straw (WCP49)	
		Tensile Index (J/g)	%Change	Tensile Index (J/g)	%Change
Initial value	1	60.74		35.91	
Untreated	2	48.34		35.27	
	3	34.73		34.56	
	5	33.29		33.29	
Alkali treated	2			36.76	4.22
	3	32.75	-5.70	36.81	6.51
	5	34.64	4.06	36.18	8.68
Refined	2			47.88	35.75
	3	50.21	44.57	47.87	38.51
	5	47.02	41.24	45.90	37.88
Alkali treated plus Refined	2			43.90	24.47
	3	47.76	37.52	47.87	38.51
	5	44.80	34.57	41.10	23.46
R48 Fraction	2	27.93		36.47	
	3	32.01		37.29	
	5	30.79		37.93	
R100 Fraction	2	29.93		39.30	
	3	29.48			
	5	29.16		34.77	
Fines Fraction P48/R250	2			34.08	-3.37
	3	39.26	13.04		
	5	38.02	14.21		
Refined R48 Fraction	2			49.46	35.62
	3	53.60	67.45	56.24	50.82
	5	57.59	87.04		
Fractionated Mixed Pulp (FMP)	2			43.66	23.79
	3	43.49	25.22	48.31	39.79
	5	44.30	33.07		

Table- A3.5: Effect on burst index of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56) Burst Index Kpa m^2/g	Bagasse (BCP56) %Change	Wheat straw (WCP49) Burst Index Kpa m^2/g	Wheat straw (WCP49) %Change
Initial value	1	3.65		2.20	
Untreated	2	2.96		2.01	
	3	1.92		2.08	
	5	1.58		1.89	
Alkali treated	2			1.95	-2.99
	3	1.61	-16.15	2.01	-3.37
	5	1.97	24.68	1.81	-4.23
Refined	2			3.07	52.74
	3	3.30	71.88	2.98	43.27
	5	2.99	89.24	2.80	48.15
Alkali treated plus Refined	2			2.52	25.37
	3	2.84	47.92	2.52	21.15
	5	2.95	86.71	2.52	33.33
R48 Fraction	2	1.22		1.99	
	3	0.98		2.14	
	5	1.01		2.24	
R100 Fraction	2	1.04		1.92	
	3	0.87			
	5	0.81		2.08	
Fines Fraction P48/R250	2			1.24	-38.31
	3	1.16	-39.58		
	5	1.00	-36.71		
Refined R48 Fraction	2			3.76	88.94
	3	4.29	337.76	4.14	93.46
	5	4.14	309.90		
Fractionated Mixed Pulp (FMP)	2			2.66	32.34
	3	2.46	28.13	2.40	15.38
	5	2.28	44.30		

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Table- A3.6: Effect on tear index of various treatments on recycled pulps.

		Bagasse (BCP56)		Wheat straw (WCP49)	
Treatment	Cycle No.	Tear Index (mN m^2/g)	%Change	Tear Index (mN m^2/g)	%Change
Initial value	1	3.93		4.35	
Untreated	2	4.28		4.21	
	3	4.42		4.25	
	5	4.23		4.40	
Alkali treated	2			4.41	4.75
	3	4.94	11.76	4.36	2.59
	5	5.06	19.62	4.54	3.18
Refined	2			4.15	-1.43
	3	4.58	3.62	4.05	-4.71
	5	5.03	18.91	4.20	-4.55
Alkali treated plus Refined	2			4.14	-1.66
	3	4.81	8.82	4.38	3.06
	5	5.06	19.62	4.60	4.55
R48 Fraction	2	5.41		6.14	
	3	5.30		6.58	
	5	5.25		6.12	
R100 Fraction	2	5.53		5.76	
	3	5.21			
	5	5.40		5.79	
Fines Fraction P48/R250	2			2.75	-34.68
	3	2.27	-48.64		
	5	2.28	-46.10		
Refined R48 Fraction	2			6.51	6.03
	3	6.09	14.91	6.52	-0.91
	5	6.31	20.19		
Fractionated Mixed Pulp (FMP)	2			4.69	11.40
	3	4.46	0.90	4.54	6.82
	5	4.59	8.51	4.41	4.75

Table- A3.7: Effect on zero-span tensile index of various treatments on recycled pulps.

Treatment	Cycle No.	Bagasse (BCP56) Zero-span Ten. In.	Bagasse (BCP56) %Change	Wheat straw (WCP49) Zero-span Ten. In.	Wheat straw (WCP49) %Change
Initial value	**1**	92.54		68.41	
Untreated	2	86.66		66.89	
	3	75.80		66.57	
	5	74.10		67.12	
Alkali treated	2			64.71	-3.26
	3	77.16	1.79	68.57	3.00
	5	75.72	2.19	67.31	0.28
Refined	2			81.94	22.50
	3	87.70	15.70	78.64	18.13
	5	86.85	17.21	78.82	17.43
Alkali treated plus Refined	2			75.61	13.04
	3	89.44	17.99	71.75	7.78
	5	86.50	16.73	71.61	6.69
R48 Fraction	2	77.21		78.20	
	3	78.92		77.87	
	5	78.96		77.22	
R100 Fraction	2	81.03		77.77	
	3	77.01			
	5	69.72		76.49	
Fines Fraction P48/R250	2			62.81	-6.10
	3	68.11	-10.15		
	5	64.09	-13.51		
Refined R48 Fraction	2			97.24	24.35
	3	95.73	21.30	100.76	29.40
	5	98.16	24.32		
Fractionated Mixed Pulp (FMP)	2			83.32	24.56
	3	77.45	2.18	86.62	30.12
	5	79.63	7.46		-3.26

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Table- A2.8: Tensile index and scattering coefficient of handsheets wet pressed at different pressures for chemical and semichemical pulps.

Pulp type	Pulp state	Pressing condition (Kgf/cm^2)	Tensile Index (J/g)	Scattering coefficient (Kg/m^2)	Zero-span Ten. Index (J/g)
WCP42	FAD*	1	33.85	39.62	72.71
	FAD	3	35.67	41.36	72.34
	Cycle- 5	1	31.28	45.05	68.33
	Cycle- 5	3	32.41	42.17	71.42
WCP49	FAD	1	32.92	46.65	64.94
	FAD	3	34.65	43.08	64.73
	FAD	6	37.38	39.96	64.23
	FAD	8	39.23	37.54	69.23
	Cycle- 5	1	30.82	47.24	61.75
	Cycle- 5	3	31.74	43.87	63.18
	Cycle- 5	6	35.63	41.62	66.06
	Cycle- 5	8	35.35	40.26	64.83
WSCP60	FAD	1	52.05	24.10	95.95
	FAD	3	52.50	21.31	92.09
	FAD	6	58.73	19.92	91.58
	FAD	8	59.58	19.36	93.39
BCP56	FAD	1	30.31	32.73	74.27
	FAD	3	37.96	30.53	74.03
	FAD	5	37.98	29.16	79.33
	FAD	8	40.29	27.22	82.45
	Cycle- 5	1	29.12	33.09	75.87
	Cycle- 5	3	34.71	31.07	75.09
	Cycle- 5	6	37.43	28.18	77.46
	Cycle- 5	8	35.22	27.25	81.31
BCP65	FAD	1	28.42	29.67	76.34
	FAD	3	31.23	27.87	76.87

* FAD- Freely air-dried pulp before recycling

Appendix- 4

BIO-DATA

CANDIDATE'S NAME	:	**MAYANK GARG**
FATHER'S NAME	:	Sh. B. B. GARG
AGE & DATE OF BIRTH	:	JUNE 4, 1969
CITIZENSHIP	:	INDIAN
ADDRESS	:	30/38A, New Adarsh Nager New Hardwar Road Vishwa bal Mandir Jr. High School Roorkee – 247667 (Uttranchal) Ph. (01332) 273156

ACADEMICS

Qualification	**Board/ University**	**%age**	**Div./Class**	**Year**
B.Sc.	Meerut University, Meerut	60	I Div.	1987
B.E. (Mechanical)	Nagpur University, Nagpur	61	I Div.	1993
M.E. (Pulp & Paper) **Received University Medal**	University of Roorkee, Roorkee	79.5	I Class First	1998
Ph.D (Pulp & Paper)	IIT, Roorkee	Registered in Jan. 1999		

M.E. Specifics

Term Paper & Seminar

"A Design correlation for the flow of pulp suspension in pipes."

Thesis

"Printability of hardwood and Nonwood Papers"

Ph.D. Topic

"Evaluation of Recycling Potential of Paper Making Fibers"

Appendix 4

Publications

1. Comparison of Printability of Hardwood and Bagasse Papers with Softwood Papers. (IPPTA Journal)
2. Response of Offset News Inks to Deinking. (IPPTA Journal)
3. Recycling Potential of Wheat Straw Pulp. (IPPTA Journal)
4. On the Use of Ink Transfer Parameters for Characterization of Printing papers. (Communicated)

Job Experience

1. **M/S Malloya's India, Nunhai, Agra**
   (Manufacturer of Diesel Engine & Generator sets)
   From June 1993 to April 1996 work as an Engineer
2. Worked as **Senior Research Fellow**, fellowship awarded by CSIR, New Delhi, under same topic. From April 01, 1999 to March 31, 2003.