

**CHEMICAL CHARACTERISATION AND THE  
EFFECT OF ALKALINE PULPING OF  
MALAYSIA CULTIVATED KENAF**  
*(Hibiscus cannabinus)*

**ANG LIN SUAN**

**UNIVERSITI SAINS MALAYSIA**

**2010**

**CHEMICAL CHARACTERISATION AND THE  
EFFECT OF ALKALINE PULPING OF  
MALAYSIA CULTIVATED KENAF  
(*Hibiscus cannabinus*)**

**By**

**ANG LIN SUAN**

**Thesis submitted in fulfillment of the requirements for the  
Degree of Master of Science**

**March 2010**

## ACKNOWLEDGEMENTS

I would like to express my gratitude appreciation to the following person for those who had kindly helped me throughout my research.

Appreciation must first be sincerely expressed to my supervisor Dr. Leh Cheu Peng for her valuable guidance, advice and encouragement throughout this study.

Special thanks to En. Abu Mangsor Mat Sari, En. Raja Khairul Azmi and En. Azli Sufryzal Bunizan, the lab assistants in the field of Bio-resource, Paper and Coating at School of Industrial Technology, for their helpful assistance in educating me the skills on all the instruments used and construction of the apparatus required, that was of great help in my research.

The financial support for this research was provided by Nibong Tebal Paper Mill Sdn. Bhd. (Project Production of Pulp and Paper from Kenaf) and Universiti Sains Malaysia through a USM Fellowship is most gratefully acknowledged. A special word of thank again to appreciation to Mr Frankie Lee Chong Chat from Nibong Tebal Paper Mill Sdn. Bhd. for supplying the raw material required for my research.

Thanks to all my friends, especially Ng Soo Huey, Milly Loo Mei Li, Koay Ee Ling, Boon Jia Geng and Beh Peng Kwang who have always had time to hear my problems and have been beside me during all the difficult times. Finally, I would like to express my lovely parent and all of my family members for their good patience, encouragement and love.

Thanks to all of you.

ANG LIN SUAN

MARCH 2010

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENTS .....</b>	<b>ii</b>
<b>TABLE OF CONTENTS .....</b>	<b>iii</b>
<b>LIST OF TABLES .....</b>	<b>viii</b>
<b>LIST OF FIGURES .....</b>	<b>x</b>
<b>LIST OF ABBREVIATIONS AND SYMBOLS .....</b>	<b>xiii</b>
<b>ABSTRAK .....</b>	<b>xvii</b>
<b>ABSTRACT.....</b>	<b>xix</b>
<b>1 INTRODUCTION .....</b>	<b>1</b>
1.1 Objectives .....	4
<b>2 LITERATURE REVIEW .....</b>	<b>5</b>
2.1 Raw material for papermaking.....	5
2.1.1 Wood resources .....	6
2.1.2 Non-wood resource.....	8
2.2 Chemical composition and its effect on papermaking .....	11
2.2.1 Carbohydrates .....	12
2.2.2 Lignin.....	14
2.2.3 Extractive.....	16
2.2.3 (a) Alcohol-benzene extractives .....	16
2.2.3 (b) 1% NaOH solubility.....	17
2.2.3 (c) Hot water solubility.....	18
2.2.4 Inorganic content .....	18

2.3 Kenaf.....	19
2.3.1 Factors effecting kenaf fibre’s properties .....	20
2.3.2 Production of pulp and paper from kenaf .....	22
2.4 Overview of pulping methods.....	26
2.4.1 Mechanical pulping .....	26
2.4.2 Chemical Pulping.....	27
2.4.3 Hybrid Pulping.....	28
2.5 Development of alkaline pulping.....	29
2.5.1 Chemical reactions of soda pulping.....	31
2.5.1 (a) Delignification reactions .....	32
2.5.1 (b) Reactions of carbohydrates .....	33
2.5.2 Chemical reactions of kraft pulping.....	35
2.5.2 (a) Reactions of lignin .....	35
2.5.2 (b) Reactions of carbohydrates .....	38
2.5.3 Addition of AQ in soda pulping .....	39
2.5.4 Identification of pulping condition .....	41
2.5.5 Alkaline peroxide mechanical pulping (APMP).....	43
2.6 Experimental design.....	46
2.6.1 Two-level factorial design .....	46
2.6.1 (a) Full factorial.....	47
2.6.1 (b) Fractional factorial.....	47
<b>3 MATERIALS AND METHODS .....</b>	<b>49</b>
3.1 Preparation of raw material.....	49
3.1.1 Samples for chemical analysis.....	49
3.1.2 Samples for pulping.....	49
3.1.3 Determination of moisture content of raw material .....	50
3.2 Analysis of chemical composition .....	50
3.2.1 Extractive content .....	50
3.2.1 (a) Alcohol-toluene solubility.....	50
3.2.1 (b) Hot water solubility .....	51
3.2.1 (c) One percent sodium hydroxide solubility .....	51

3.2.2 Ash content.....	51
3.2.3 Acid insoluble lignin.....	52
3.2.4 Holocellulose content .....	52
3.2.5 Alpha-cellulose content .....	53
3.2.6 Beta- and gamma- cellulose content.....	54
3.2.7 Carbohydrate composition by gas chromatograph .....	54
3.3 Microscopy analysis of fibre.....	56
3.4 Pulping method .....	57
3.4.1 Chemical pulping.....	57
3.4.1 (a) Preparation and standardisation of 2M sodium hydroxide.....	57
3.4.1 (b) Procedure of chemical pulping .....	57
3.4.2 Alkaline pre-impregnation.....	59
3.4.3 Alkaline peroxide mechanical pulping (APMP).....	59
3.4.3 (a) Experimental design for the APMP .....	59
3.4.3 (b) Preparation and standardisation of hydrogen peroxide.....	60
3.4.3 (c) Procedure of APMP .....	61
3.5 Pulp properties .....	62
3.5.1 Kappa number.....	62
3.5.1 (a) Preparation and standardisation of 0.1N potassium permanganate.....	62
3.5.1 (b) Preparation and standardisation of 4N sulfuric acid .....	63
3.5.1 (c) Preparation and standardisation of 0.1N sodium thiosulfate.....	63
3.5.1 (d) Procedure of kappa number determination .....	64
3.5.2 Pulp viscosity.....	65
3.5.3 Canadian standard freeness (CSF).....	66
3.6 Handsheet making.....	66
3.6.1 Preparation of pulp stock.....	67
3.6.2 Determination of pulp stock consistency.....	67
3.6.3 Procedure of handsheet making.....	67
3.7 Handsheet testing.....	68
3.7.1 Physical testing .....	69
3.7.1 (a) Grammage.....	69
3.7.1 (b) Thickness .....	69
3.7.2 Optical testing.....	70

3.7.2 (a) Opacity test .....	70
3.7.2 (b) Brightness test.....	70
3.7.3 Mechanical testing .....	70
3.7.3 (a) Tensile test .....	70
3.7.3 (b) Tearing test .....	71
3.7.3 (c) Burst test .....	71
3.7.3 (d) Folding test .....	71
<b>4 RESULTS AND DISCUSSION .....</b>	<b>72</b>
4.1 Comparison of chemical composition.....	72
4.1.1 Extractive content .....	73
4.1.2 Ash content .....	75
4.1.3 Acid insoluble lignin.....	76
4.1.4 Holocellulose content .....	76
4.1.5 Alpha-Cellulose content .....	77
4.1.6 Carbohydrate composition by gas chromatography .....	78
4.2 Microscopic appearance of kenaf .....	79
4.3 Alkaline chemical pulping .....	81
4.3.1 Effects of soda-AQ pulping variables on kenaf bast fibre.....	82
4.3.1 (a) Effects of active alkali (AA) .....	82
4.3.1 (b) Effects of cooking temperature.....	86
4.3.1 (c) Effects of the ratio of liquor to material (L: M).....	90
4.3.2 Effects of alkaline pre-impregnation on kenaf bast fibre.....	93
4.3.3 Comparison between soda-AQ, kraft and kraft-AQ pulping on kenaf bast fibre	98
4.3.4 Effects of soda-AQ pulping on kenaf core fibre.....	99
4.3.5 Comparison between kenaf bast and core fibres on soda-AQ pulping .....	101
4.4 Statistical study on alkaline peroxide treatment.....	103
4.4.1 Regression analysis.....	106
4.4.2 Model validation.....	109
4.4.3 Transformation of response .....	115
4.4.4 Analysis of chemical treatment variables .....	118
4.4.4 (a) Effects on pulping yield .....	118

4.4.4 (b) Effects on brightness.....	120
4.4.4 (c) Effects on tensile index .....	122
4.4.4 (d) Effects on tear index .....	124
4.4.4 (e) Effects on burst index .....	125
4.4.5 Verification of factorial models.....	126
<b>5 CONCLUSION .....</b>	<b>127</b>
<b>6 RECOMMENDATIONS.....</b>	<b>129</b>
<b>REFERENCES.....</b>	<b>130</b>
<b>APPENDICES.....</b>	<b>138</b>



## LIST OF TABLES

Table 2.1:	Example of fibre materials (Hurter., 1997; Ince, 2004; Rodríguez et al., 2008; Wanrosli et al., 2007)	5
Table 2.2:	Silicate content of raw material	11
Table 2.3:	Chemical composition of non-woods and woods	12
Table 2.4:	Changes in chemical composition of kenaf bast fibre with the growing time (Rowell et al., 2000)	21
Table 2.5:	Changes in fibre physical properties of kenaf with the growing season (Rowell and Stout, 1998; Rowell et al., 2000)	21
Table 2.6:	Variations in chemical composition of kenaf between top and bottom portion (Rowell et al., 2000)	22
Table 2.7:	Soda-AQ pulping conditions and result of pulp properties for kenaf whole stalk and bast	42
Table 3.1:	Calibration weights of standard sugars for carbohydrate content analysis	55
Table 3.2:	Pulping conditions used for kenaf bast and kenaf core	58
Table 3.3:	Pulping conditions from the factorial design of the experiments	60
Table 3.4:	Experimental variables used in both actual and coded ranges	60
Table 4.1:	Chemical compositions of kenaf bast, core and whole stalk grown in penang compared with published data from different locations (all values presented as percent of oven-dry raw materials)	72
Table 4.2:	Polysaccharide of holocelluloses of kenaf bast, core and whole stalk	78
Table 4.3:	Alkaline chemical pulping conditions and the pulp properties of kenaf bast and core fibres	81
Table 4.4:	Physical properties of handsheet from kenaf bast and kenaf core pulps	82
Table 4.5:	Results of $\alpha$ , $\beta$ and $\gamma$ -cellulose of kenaf bast resultant pulps with and without pre-impregnation	97

Table 4.6:	Experimental conditions used in alkaline peroxide treatment of kenaf core in both coded and actual variable level and the results for the pulping and handsheet properties	107
Table 4.7:	Statistical assessment of variables to responses	108
Table 4.8:	Statistical analysis of reduce models of responses	108
Table 4.9:	Statistical assessments of transformed model of tear and burst indices	115
Table 4.10:	Statistical analysis of transformed reduce models of tear and burst indices	115
Table 4.11:	Experimental conditions for validation of factorial models	126
Table 4.12:	Comparison between predicted and actual experimental values of the five responses	126

## LIST OF FIGURES

Figure 2.1:	World wood pulp consumption in 2004 (Whiteman, 2005)	6
Figure 2.2:	Diagram showing types of hardwood and softwood cells (Becwar et al., 1988)	7
Figure 2.3:	Production of world non-wood pulp capacity (FAO)	9
Figure 2.4:	Producer of world non-wood pulp capacity in 1997 (FAO, 1997-2002)	9
Figure 2.5:	Raw material sources for non-wood pulp in 2002 (FAO)	10
Figure 2.6:	Chemical precursors of lignin (Britt, 1970; Fengel and Wegener, 1989; Lewin, 1991; Rowell et al., 2000)	15
Figure 2.7:	Cleavage of phenolic $\alpha$ -aryl ether bonds in soda pulping (Sjöström, 1993)	32
Figure 2.8:	Cleavage of non-phenolic $\beta$ -aryl ether bonds in soda pulping (Sjöström, 1993)	33
Figure 2.9:	Peeling (a) and stopping (b) reactions of cellulose (Sjöström, 1993)	34
Figure 2.10:	Alkaline hydrolysis of cellulose (Casey, 1980)	35
Figure 2.11:	Formation of a stilbene structure from phenyl coumaran in alkali (Sjöström, 1993)	36
Figure 2.12:	Main reactions of the phenolic $\beta$ -aryl ether structures in kraft pulping (Walker, 2006)	37
Figure 2.13:	Examples of condensation reactions during kraft pulping (Sjöström, 1993)	37
Figure 2.14:	Formation of hexenuronic acids during kraft pulping (Jiang et al., 2000)	38
Figure 2.15:	Anthraquinone-anthrahydroquinone reactions with carbohydrates in soda pulping (Dimmel et al., 2003)	40
Figure 2.16:	Cleavage of $\beta$ -aryl ether bonds in soda pulping by anthrahydroquinone with regeneration of anthraquinone (Sjöström, 1993)	40
Figure 3.1:	Division of sheets for testing	69

Figure 4.1:	SEM micrographs of the kenaf bast and core: (a) fibres bundles in kenaf bast; (b) fibres with simple pits (upper part) and spiral thickening (lower part) in inner woody core; (c) spiral thickening; (d) fibres (upper part) and polygonal shaped parenchymatous pith (lower part); (e) and (f) fibres of woody core and parenchymatous pith, respectively. Magnification = 200 x except 400 x for (c) and 50 x for (e)	80
Figure 4.2:	Effects of active alkali on handsheet properties	85
Figure 4.3:	Effects of cooking temperature on handsheet properties	90
Figure 4.4:	Effects of ratio to material (L : M) on handsheet properties	93
Figure 4.5:	Effects of pre-impregnation on handsheet properties	96
Figure 4.6:	SEM micrographs of the kenaf bast's handsheet: (1a) and (1b) without pre-impregnation; (2a) and (2b) with 0.25M NaOH pre-impregnation. Magnification = 100x for (1a) and (2a); 1.0k for (1b) and (2b)	97
Figure 4.7:	Effects of soda-AQ, kraft and kraft-AQ pulping on handsheet properties	99
Figure 4.8:	Effects of kenaf core soda-AQ pulping on handsheet properties	100
Figure 4.9:	Comparison between kenaf bast and kenaf core soda-AQ pulping on handsheet properties	102
Figure 4.10:	SEM micrographs of handsheets made from soda-AQ pulps for kenaf bast (a, 50x and b, 300x) and kenaf core (c, 50x and d, 300x)	102
Figure 4.11:	A half normal probability plot of pulping yield	103
Figure 4.12:	A half normal probability plot of ISO brightness	104
Figure 4.13:	A half normal probability plot of tensile index	104
Figure 4.14:	A half normal probability plot of tear index	105
Figure 4.15:	A half normal probability plot of burst index	105
Figure 4.16:	Normal probability plot of the studentized residuals of pulping yield	110
Figure 4.17:	Normal probability plot of the studentized residuals of ISO brightness	110
Figure 4.18:	Normal probability plot of the studentized residuals of tensile index	111
Figure 4.19:	Normal probability plot of the studentized residuals of tear index	111

Figure 4.20:	Normal probability plot of the studentized residuals of burst index	112
Figure 4.21:	Studentized residuals versus predicted values of pulping yield	112
Figure 4.22:	Studentized residuals versus predicted values of ISO brightness	113
Figure 4.23:	Studentized residuals versus predicted values of tensile index	113
Figure 4.24:	Studentized residuals versus predicted values of tear index	114
Figure 4.25:	Studentized residuals versus predicted values of burst index	114
Figure 4.26:	Transformed normal probability plot of the studentized residuals of tear (a) and burst indices (b)	116
Figure 4.27:	Transformed studentized residuals versus predicted values of tear (a) and burst indices (b)	117
Figure 4.28:	Interaction plot of pulping yield as a function of NaOH and stabilizer at constant H <sub>2</sub> O <sub>2</sub> (1.75%), without the addition of DTPA	119
Figure 4.29:	3D response surface plot of ISO brightness as a function of NaOH and H <sub>2</sub> O <sub>2</sub> without the addition of stabilizer and DTPA	120
Figure 4.30:	Interaction plot of ISO brightness as a function of stabilizer and DTPA at constant H <sub>2</sub> O <sub>2</sub> (1.75%) and NaOH (4.00%)	122
Figure 4.31:	3D response surface plot of tensile index as a function of NaOH, H <sub>2</sub> O <sub>2</sub> and stabilizer without the addition of DTPA	123
Figure 4.32:	3D response surface plot of tear index as a function of NaOH, H <sub>2</sub> O <sub>2</sub> and stabilizer without the addition of DTPA	124
Figure 4.33:	Interaction plot of burst index as a function of NaOH and stabilizer at constant H <sub>2</sub> O <sub>2</sub> (1.75%), without the addition of DTPA	125

## LIST OF ABBREVIATIONS AND SYMBOLS

%	percentage
(-)	low level
(+)	high level
±	about
=	equals
$\alpha$	alpha
AA	Active Alkali
AHQ	Anthrahydroquinone
ANOVA	Analysis of Variance
APMP	Alkaline Peroxide Mechanical Pulping
AQ	Anthraquinone
ARS	Agricultural Research Service
ASAM	Alkaline Sulphite-Anthraquinone-Methanol
AS-AQ	Alkaline Sulphite-Anthraquinone
$\beta$	Beta
BCTMP	Bleached Chemithermomechanical pulp
C	Chlorination stage
C+	with addition of stabilizer
C-	without addition of stabilizer
°C	Degree Celcius
CED	Cupriethylenediamine
cP	Centipoise
CSF	Canadian Standard Freeness
CTMP	Chemi-Thermo-Mechanical Pulp

CMP	Chemimechanical pulp
D+	with addition of DTPA
D-	without addition of DTPA
DAP	Days After Planting
DP	Degree of Polymerisation
DTPA	Diethylene Triamine Pentaacetic Acid
EDTA	Ethylene Diamine Tetraacetic Acid
EFB	Oil palm Empty Fruit Bunch
edn.	edition
Eq.	Equation
FAO	Food and Agriculture Organization
GC	Gas Chromatography
$\text{g/m}^2$	Grammage
$\cdot\text{OH}$	Hydroxyl radical
$\text{HOO}^-$	Perhydroxyl anion
$\text{H}_2\text{O}_2$	Hydrogen peroxide
$\text{H}_2\text{O}$	Molecular water
$\text{HS}^-$	Hydrosulfide
$\text{H}_2\text{SO}_3$	Sulfurous acid
$\text{H}_2\text{SO}_4$	Sulfuric acid
$\text{HSO}_3^-$	Bisulfite ion
ISO	International Organisation for Standardization
KHP	Potassium hydrogen phthalate
KI	Kenaf International
KI	Potassium iodida
$\text{KIO}_3$	Potassium iodate

$\text{KMnO}_4$	Potassium permanganate
kPa	kilopascal
L	liter
M	Molarity
m	meter
$\text{MgSO}_4$	Magnesium sulfate
ml	mililitre
mm	milimetre
MP7	7 <sup>th</sup> Malaysia Plan 1996-2000
MP9	9 <sup>th</sup> Malaysia Plan 2006-2010
MPa	Mega Pascal
N	Newton
N	Normality
$\text{Na}^+$	Sodium ion
$\text{Na}_2\text{C}_2\text{O}_4$	Sodium oxalate
$\text{NaClO}_2$	Sodium Chlorite
$\text{NaOH}$	Sodium hydroxide
$\text{Na}_2\text{O}$	Sodium oxide
$\text{Na}_2\text{S}$	Sodium sulfide
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	Sodium thiosulfate pentahydrate
$\text{Na}_2\text{SiO}_3$	Sodium silicate
$\text{Na}_2\text{SiO}_3 + \text{MgSO}_4$	Addition sodium silicate with magnesium sulfate
$\text{Na}_2\text{SO}_3$	Sodium sulfite
$\text{NaSO}_4$	Sodium sulfate
$\text{Na}_2\text{CO}_3$	Sodium carbonate
NSSC	Neutral Sulphite Semi-Chemical



O <sub>2</sub>	Molecular oxygen
O <sub>2</sub> <sup>•-</sup>	Superoxide anion radical
OH <sup>-</sup>	Hydroxide ion
OECD	Organisation for Economic Co-operation and Development
P	Primary cell wall
PGW	Pressure Groundwood
P-RC	Preconditioning followed by refiner chemical treatment
PRMP	Pressurized Refiner Mechanical Pulping
psi	pascal
Sdn Bhd	Sendirian Berhad
NTA	Nitrilotriacetic acid
R <sup>2</sup>	Squared correlation coefficient
RH	Humidity
RMP	Refiner Mechanical Pulp
Rpm	round per meter
S1	Outer layer secondary cell wall
SEM	Scanning Electron Microscope
SGW	Stone Groundwood
TAPPI	Technical Association of Pulp and Paper Industry
TMP	Thermo-Mechanical Pulping
USDA	United States Department of Agricultural

**PENCIRIAN KIMIA DAN KESAN PEMULPAAN ALKALI TERHADAP KENAF  
(*HIBISCUS CANNABINUS*) YANG DITANAM DI MALAYSIA**

**ABSTRAK**

Satu kajian menyeluruh telah dijalankan terhadap komposisi kimia bagi bast dan core *Hibiscus cannabinus* (kenaf) yang ditanam di Malaysia. Perubahan-perubahan dalam komposisi kimia bagi keseluruhan batang kenaf pada umur pertumbuhan yang berbeza juga dikaji. Dalam perbandingan kenaf yang ditanam di Malaysia dan negara-negara yang berlainan, kenaf tanaman tempatan (Pulau Pinang) menunjukkan beberapa perbezaan dalam nilai-nilai komposisi kimia. Peningkatan umur pertumbuhan kenaf dari 15 ke 19 minggu didapati menurunkan kandungan ekstraktif secara positif, tetapi meningkatkan kandungan lignin dan menurunkan kandungan holoselulosa secara negatif. Berdasarkan keputusan-keputusan bagi pelbagai pemulpaan soda-AQ, adalah didapati tahap degradasi karbohidrat dan pendeligninan akan meningkat dengan peningkatan alkali aktif dan suhu pemasakan, tetapi tahap-tahap itu akan menurun dengan peningkatan nisbah liquir kepada bahan mentah (L: M). Sifat-sifat pulpa dan kertas daripada kenaf bast yang paling memuaskan boleh diperolehi dengan menggunakan 19.4% alkali aktif bersama 0.1% AQ dan 7:1 nisbah L: M selama 2 jam pada 160°C. Selain daripada itu, pra-impregnasi alkali berkepekatan rendah sebelum pemulpaan soda-AQ bukan sahaja boleh meningkatkan kelikatan pulpa dengan berkesan, tetapi juga nyata sekali meningkatkan ciri-ciri kekuatan kertas, terutama ketahanan lipatan, indeks tensil dan indeks pecahan. Antara tiga jenis process masakan beralkali (kraft, kraft-AQ dan soda-AQ), keputusan bagi sifat-sifat pulpa dan kertas menunjukkan bahawa pulpa soda-AQ adalah setanding atau berkualiti lebih tinggi daripada pulpa kraft dan kraft-AQ. Kajian juga mendapati di antara kertas soda-AQ kenaf bast dan core, sifat-sifat kekuatan kertas kenaf core adalah mengejutkan, oleh kerana sifat-sifat kekuatan kertas kenaf core adalah lebih tinggi daripada kenaf bast. Bagaimanapun, kenaf core menunjukkan hasil penskrinan yang lebih rendah daripada kenaf bast. Sebaliknya, kesan daripada empat

pembolehubah-pembolehubah kimia (NaOH, H<sub>2</sub>O<sub>2</sub>, penstabil (Na<sub>2</sub>SiO<sub>3</sub> MgSO<sub>4</sub>) dan DTPA) bagi pemulpaan mekanikal peroksida beralkali kenaf core dan interaksi bagi lima sambutan—hasil pemulpaan, kecerahan ISO, indeks tensil, indeks koyakan dan indeks pecahan telah dinilai secara statistik melalui dua tahap faktorannya penuh rekabentuk ujikaji dengan bantuan komputer perisian Design Expert®. Analisis statistik menunjukkan penambahan penstabil akan meningkatkan semua sifat-sifat kekuatan kertas, manakala peningkatan cas alkali akan menurunkan hasil pemulpaan dan peningkatan cas hidrogen peroksida akan meningkatkan kecerahan pulpa. Semua rekabentuk faktorannya yang dibina juga telah disahkan secara statistik dan eksperimental.

**CHEMICAL CHARACTERISATION AND THE EFFECT OF ALKALINE  
PULPING OF MALAYSIA CULTIVATED KENAF (*HIBISCUS CANNABINUS*)**

**ABSTRACT**

A comprehensive study is carried out on the chemical composition of the bast and core of the *Hibiscus cannabinus* (kenaf) cultivated in Malaysia. The changes in the whole stalk chemical composition due to different plant age are also examined. In comparison to the kenaf planted in Malaysia and different countries, the locally planted kenaf (Penang) shows some differences in the value of the chemical composition. Increase of plant age from 15 to 19 weeks of kenaf growth are positively decreases the extractive content, but negatively increases the lignin content and decreases the holocellulose content. Based on the results of various soda-AQ pulping, it is found that the carbohydrate degradation and delignification degree increases with the increase of active alkali and cooking temperature, but the degree decreases with the increase of liquor to material (L: M) ratio. The most satisfactory properties of pulp and handsheets from kenaf bast can be attained by employing 19.4% active alkali with 0.1% AQ and L: M ratio of 7:1 cooked for 2 hours at 160°C. Besides, mild alkaline pre-impregnation prior soda-AQ pulping does not only effectively improve the pulp viscosity, but it also substantially increased the handsheets' strength properties, especially folding endurance, tensile and burst indices. Among the three alkaline cooking processes (kraft, kraft-AQ and soda-AQ), the results of pulp and handsheet properties shows that the soda-AQ pulp is comparable or even slightly of higher quality than the kraft and kraft-AQ pulps. The study also found that between the kenaf bast and core soda-AQ handsheets, the strength properties of the kenaf core's handsheet are surprisingly higher than of the kenaf bast. Nevertheless, the kenaf core shows considerable lower screened yield than kenaf bast. On the other hand, the effect of four chemical variables (NaOH, H<sub>2</sub>O<sub>2</sub>, stabilizer (NaSiO<sub>3</sub> + MgSO<sub>4</sub>) and DTPA) of the kenaf core alkaline peroxide mechanical pulping and their

interactions on the five responses—pulping yield, ISO brightness, tensile, tear and bursting indices are statistically evaluated by employing a two-level full factorial experimental design through a computer aided software named Design Expert®. The statistical analysis shows that the addition of stabilizer improve all the handsheets' strength properties, while the increase of alkaline charge decrease the pulping yield and the increase of hydrogen peroxide charge increases the pulp brightness. All the factorial designs built are also statistically and experimentally verified.

## 1 INTRODUCTION

World Resources Institute (2009) reported that the paper and paperboard demand is increasing worldwide. Over the past few decades, the paper and paperboard demand increased more than twofold, from 167 million metric tons in 1982 to 352 million metric tons in 2005. Reference Scenario published by Organisation for Economic Co-operation and Development, OECD (2001), predicted that the growth of world pulp and paper demand is about 77% from 1995 to 2020. Since 90-95% of the world pulp raw material is contributed by wood fibres, this indicated that the increase of the pulp and paper demand definitely will lead to massive deforestation and aggravates the negative impacts on the environment (Rodríguez et al., 2008).

For developed, industrialised countries, sustainable forest management is successfully implemented by using modern forest management tools to improve forest inventory and management planning (Hasenauer, 2006). For some developing countries such as Brazil, Myanmar and Indonesia, there are more than 50% of the total land area still covered by forest (EarthTrends, 2003; Santoso, 2003). However, uncontrollable illegal logging activities are frequently reported and have caused serious deforestation. Consequently, the ecological balance is altered and this contributes to climate change (Duinker et al., 1998).

Due to the decrease of wood fibre availability and the increase of wood cost, many studies have focussed on the use of alternative fibrous resources such as agricultural residues (rice and wheat straw, oil palm empty fruit bunch (EFB), sugarcane bagasse, banana stem and etc) and non-wood crop plant (kenaf, sisal, jute, hemp, bamboo and etc) as the fibre source for the pulp and paper industry (Hurter, 1997; Rodríguez et al., 2008; Wanrosli et al., 2007). As the scarcity of wood fibre is expected in the oncoming future, worldwide, and also the environmental pressure exerted by the public especially the environmental groups, non-wood plant is being recognised as a potential sustainable fibre supply, especially in countries that

wood resource is limited. One of the advantages of non-wood fibre is its short growing time to reach maturity, and also produces more usable fibre per land area than trees. For example, a non-wood fibre of kenaf and hemp has about two times higher annual yields per hectare than that of fast-growing softwoods (Pande, 1998).

Among non-wood plants, kenaf seem like it has high potential as a papermaking raw material. Kenaf is naturally pest-resistant and grows well in a wide range of climatic condition in many countries without using a large amount of herbicides and fertilizers (Paper Task Force, 1996). Furthermore, kenaf has been selected as the top potential plant for pulp and paper making by the Department of Agriculture, United State (USDA) in 1960 (Kugler, 1990). In the early 1980s, many countries such as Italy, Japan, Mexico and Brazil also foresaw the bright prospects of kenaf and thus have started kenaf research projects extensively (Taylor, 1993).

In Malaysia, kenaf is first introduced in the early 1970's and it is recognised as high potential alternative fibrous material for the production of panel products such as fibreboard and particleboard in the late 1990s, under the 7<sup>th</sup> Malaysia Plan 1996-2000 (MP7) (Malaysian Timber Council, 2005). Due to its potential commercial value, the government has allocated RM35 million for kenaf development project under the 9<sup>th</sup> Malaysia Plan 2006-2010 (MP9). Under the plan, the National Kenaf and Tobacco Board (formerly known as National Tobacco Board) contrives the development of kenaf cultivation in order to replace the current tobacco cultivation, especially in the state of Kelantan. Furthermore, instead of panel products, the government also emphasizes diversifying and commercializing the downstream kenaf-based industries including the pulp and paper industry in cooperation with the private sector (NST Business Times, 2008; Malaysian National News Agency, 2008).

Kenaf grows quickly and reaches 5-6 m in height with 25-35 mm in diameter within five to six months. Eventually, kenaf yields about 6 to 10 tons of dry fibre per acre per year (Zaveri,

2004). Kenaf stem consists of two distinct parts, the long fibres bast and the short fibres core (Kaldor et al., 1990). Besides, the fibre length, these two fibres are also greatly different in chemical compositions, and thus they are not recommended to be pulped together (Ohtani et al., 2001). An excellent strength characteristic of kenaf bast is that it is well suited for high quality specialty paper and chemical pulping is more favourable (Webber et al., 2002). In contrast to kenaf bast, kenaf core is less suitable to be cooked by chemical pulping because it is relatively more difficult to cook and the pulp resulted with higher kappa number and lower yield (Khristova, et al. 2002). Because of its high absorbency property of the woody core, it is well recognised for use as an absorbent product for either water or oil (Webber et al., 2002; Zaveri, 2004). For papermaking, kenaf core is commonly used to produce mechanical or chemi-mechanical pulps. By using appropriate chemical treatment, pulps with a brightness of 60% (Rowell et al., 1996) can be obtained by virtue of its naturally bright fibre (Rosenberg, 1996). This indicates that further bleaching is not necessary to produce low grade printing paper such as newspapers, cheap fiction and comic books.

Although many research studies on kenaf in the production of pulp and paper have been carried out extensively, studies based on locally available kenaf on pulp and papermaking are considered limited (Sharmiza et al., 2005; Ashori et al. 2005, Latifah et al., 2007). Besides, as reported, kenaf fibre properties especially its chemical components are varied due to different cultivars, years, climate and soil (Webber, 1992, Cook et al., 1998). This is very important because the differences of the kenaf fibre properties will directly influence the effect of the pulping conditions to be applied, which meant that even though under the same pulping conditions, with different chemical compositions, the properties of the resultant pulp and handsheets can possibly differ. For this, the chemical compositions of the bast and core of the locally planted kenaf are examined in this study. In addition, the effects of alkaline pulping or treatment on the separated kenaf bast and core fibres are also investigated.



## 1.1 Objectives

- To determine and to compare the chemical compositions of kenaf bast, core and two different plant age of whole stalk kenaf.
- To investigate the effects of alkaline pre-impregnation and various variables of soda-AQ pulping on the pulp and handsheet properties from kenaf bast.
- To compare the effect of various alkaline pulping processes on kenaf bast and the differences between kenaf bast and core soda-AQ pulp and handsheet properties.
- To statistically examine the effects of various variables of alkaline peroxide mechanical pulping on kenaf core by using two-level full factorial design ( $2^k$ ).

## 2 LITERATURE REVIEW

### 2.1 Raw material for papermaking

The primary component of paper is fibres of lignocellulosic materials either from wood or non-wood plant. The lignocellulosic material has to be converted into pulp through either chemical, mechanical or hybrid of these two processes before being used in paper mill (Smook, 1992; Rousu et al., 2002). Since early 20th century, wood is the major lignocellulosic material for the world virgin pulp and paper production accounting for 90-95% (Fengel and Wegener, 1989; Smook, 1992; Rodríguez et al., 2008). Other lignocellulosic materials are non-wood crop plant and agricultural residue. Besides the virgin pulp, secondary pulp from recovered fibre of various waste paper products are also used in paper production and contribute to about 45% of world pulp and paper production in 2004 (Whiteman, 2005). Examples for each of fibre source are listed in Table 2.1. Besides that, some other non-lignocellulosic materials such as metals, cement, and synthetic plastic fibres are also used in papermaking but only in a small amount and only for special applications (Ince, 2004; Kocurek and Stevens, 1983).

Table 2.1: Example of fibre materials (Hurter., 1997; Ince, 2004; Rodríguez et al., 2008; Wanrosli et al., 2007)

Source of fibres		Examples
Wood	Harwoods	Eucalyptus, acacia, birch, aspen, poplar and etc.
	Softwoods	Pine, spruce, fir, larch, tamarack and etc.
Non-wood	Non-wood crops	Jute, hemp, sisal, kenaf and etc.
	Agricultural residues	Empty fruit bunches (EFB), oil palm trunks, oil palm fronds, rice straw, sugarcane and etc.
Recovered fibres	Recycled papers	Old newspaper, corrugated board, printing paper, writing paper and etc.

### 2.1.1 Wood resources

Wood is one of the important basic components for pulp and paper industry. Today, wood pulp contributes to about 90% of the world virgin pulp production even though the first paper invented by a Chinese named Ts'ai Lun was made from non-wood plant (Hurter, 1998; Jiménez et al., 2009; Rodríguez et al., 2008; Sixta, 2006). As shown in Figure 2.1, the world wood pulp is produced by using different types of pulping method viz mechanical, chemical or semi-chemical pulping. Among the three, the chemical pulp contributes to the highest portion, which accounts for 74.3% of 171 million metric tons of the total world wood pulp for paper product in 2004. In between, the vast majority (96%) of the chemical pulp is kraft pulp. The remaining 21.0% and 4.7% of the world wood paper product are from mechanical and semi-chemical pulp respectively.

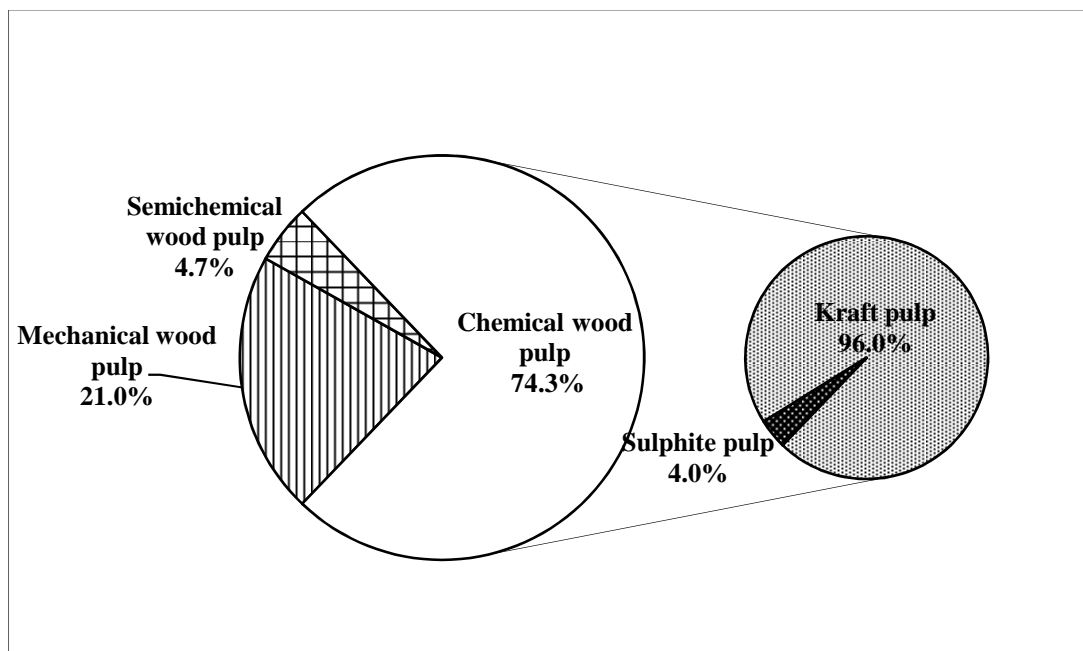


Figure 2.1: World wood pulp consumption in 2004 (Whiteman, 2005)

Pine and spruce are the first two species of softwood used in large quantities for papermaking in Europe and North America. However, during the past few decades, the plantations from all over the world has gradually evolved to hardwood species especially

eucalyptus, since their growth rate is relatively faster than softwood, which requires only seven years to reach maturity for harvesting (Sixta, 2006).

The structures of anatomy of hardwoods are more complex than softwoods. This is because hardwood is composed by a variety of different cells in the form of fibres, vessel elements or pores, tracheids and parenchyma cells. Whereas, softwood has relatively simple structure as 90-95% of its cells are tracheid, long and slender with flattened or tapered closed edges as shown in Figure 2.2. Thus, softwood is relatively a superior fibre source for papermaking (Fengel and Wegener, 1989; Walker, 2006).

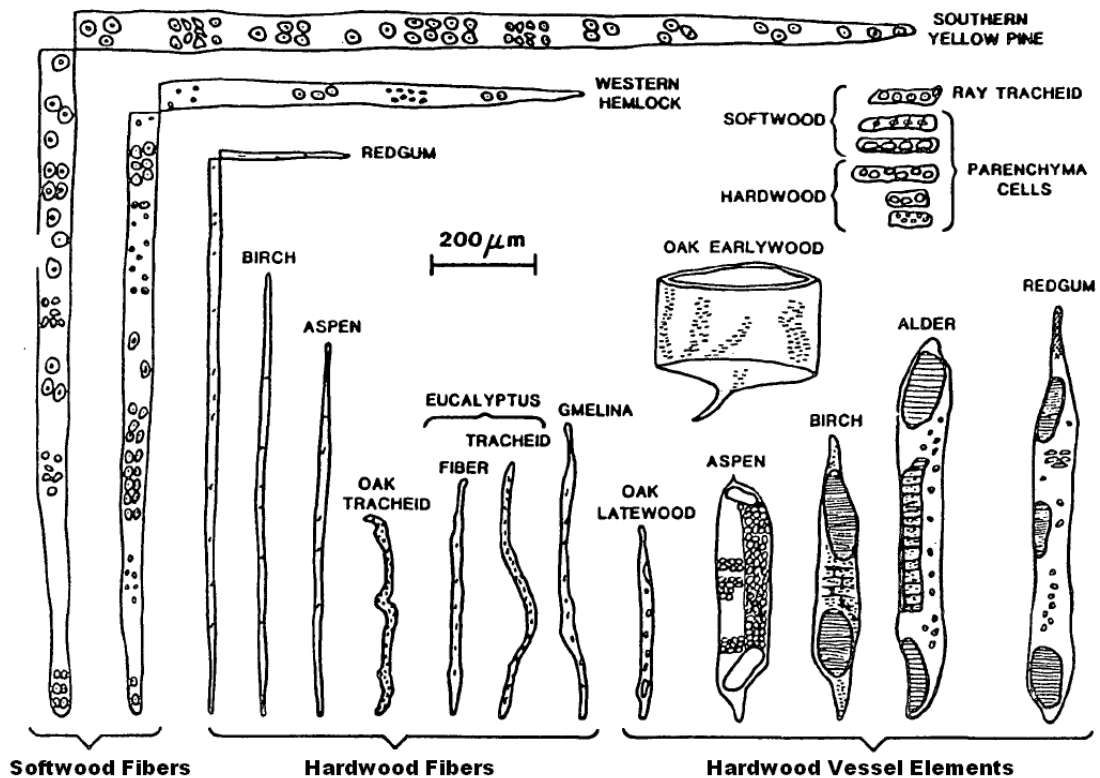


Figure 2.2: Diagram showing types of hardwood and softwood cells (Becwar et al., 1988)

Different types of raw materials normally vary in physical characteristics and hence influence their utility in papermaking. For example, hardwood fibres are generally shorter (average 0.9 to 1.5 mm) and more rigid than softwood fibres (average 3 to 3.6 mm). Hence short hardwood fibres are good for printing paper by providing smoothness and printability

properties. On the other hand, the longer softwood fibres tend to produce high strength paper (Fengel and Wegener, 1989; Ince, 2004). However, a higher beating degree is required by extremely long fibre as it may lead to a wild formation in the finished sheet. Consequently, it causes rougher surfaces and weaker strength property (Casey, 1980).

#### 2.1.2 Non-wood resource

The capacity of non-wood pulp for papermaking is increasing worldwide. According to a pulp and paper capacity survey published by Food and Agriculture Organization (FAO), over the period of 1972-1997 (Figure 2.3), the production of the world's total non-wood pulp capacity increases from 6.1% in 1972 to 10.7% in 1992, but it remains stable at 10%-11% in the following years. As shown in Figure 2.4, in 1997, China produces more than 70% of the world's non-wood pulp, followed by India which accounts for 8.3% (FAO, 1997-2002). However, the total capacity of world non-wood pulp seriously decreases for the following year, which only remains ca 1% according to FAO (1998-2005). The substantial drop of the world non-wood pulp as reported by FAO is due exclusively to China's and India's pulp and paper capacity reports, where about 80% of the non-wood pulp actually come from these two countries. Based on other reports (Whiteman, 2005) in 2004, world non-wood capacity is 19 million metric tons, still remaining about 10% of the world pulp and paper capacity. According to Figure 2.5, largest share of the non-wood fibre material used as pulp source is straw, which is 45% of world's total non-wood pulp capacity in 2002, while other fibres (including reeds, esparto, rag, etc.), bagasse and bamboo are 35%, 13.6%, and 6.4% respectively.

In papermaking, the suitable ratio of fibre length to diameter lies in the range of about 50-200:1 (Kocurek and Stevens, 1983). Since the non-wood plant's average fibre length which generally is in the range of 1 mm to 30 mm, it varies in different plant species and thus, the average length to diameter ratio is in the range of 50:1 to 1500:1 (Pahkala, 2001).

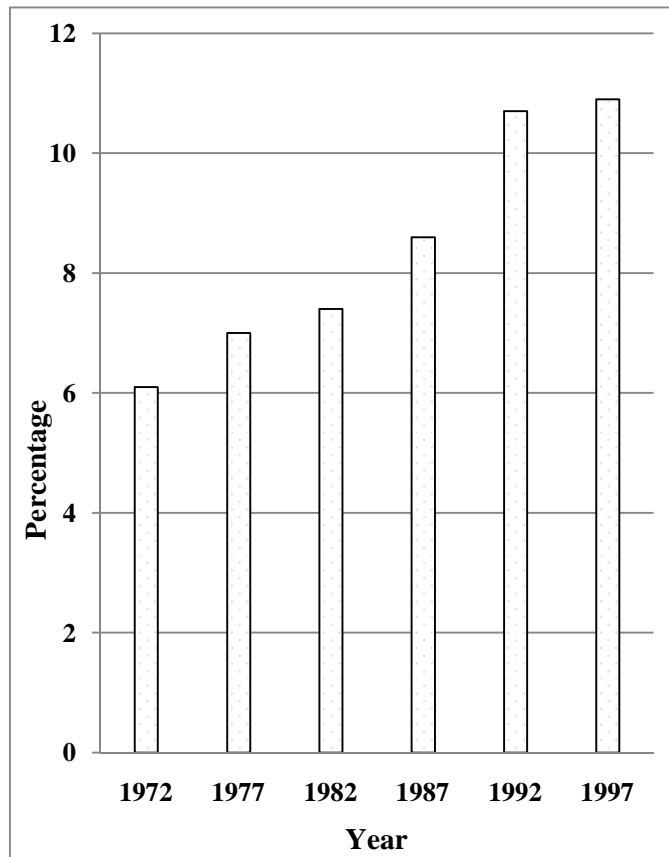


Figure 2.3: Production of world non-wood pulp capacity (FAO, 1972-2002)

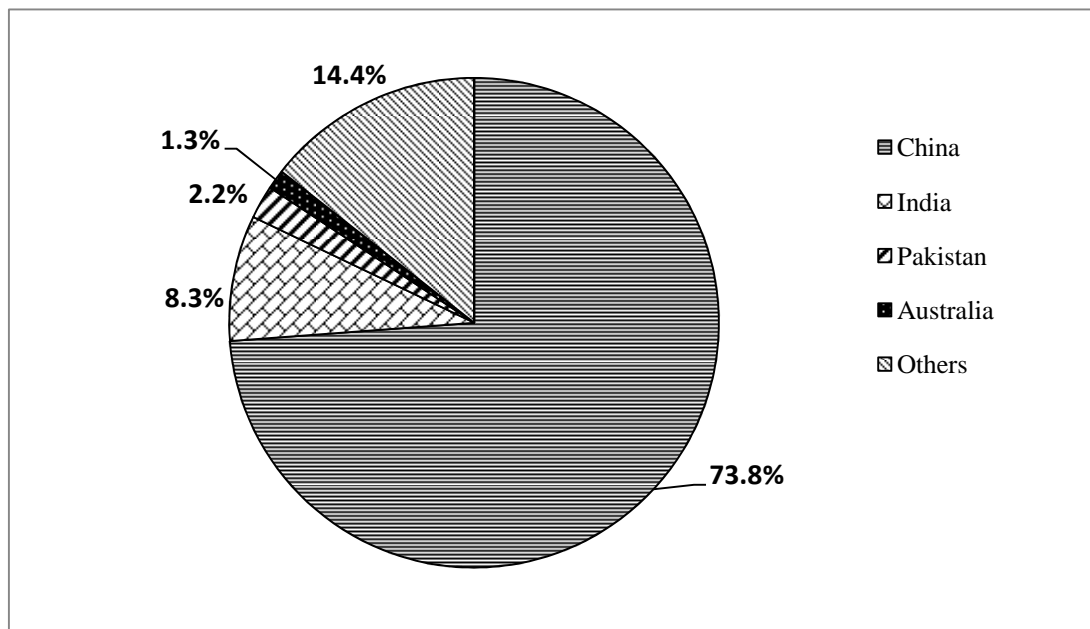


Figure 2.4: Producer of world non-wood pulp capacity in 1997 (FAO, 1997-2002)

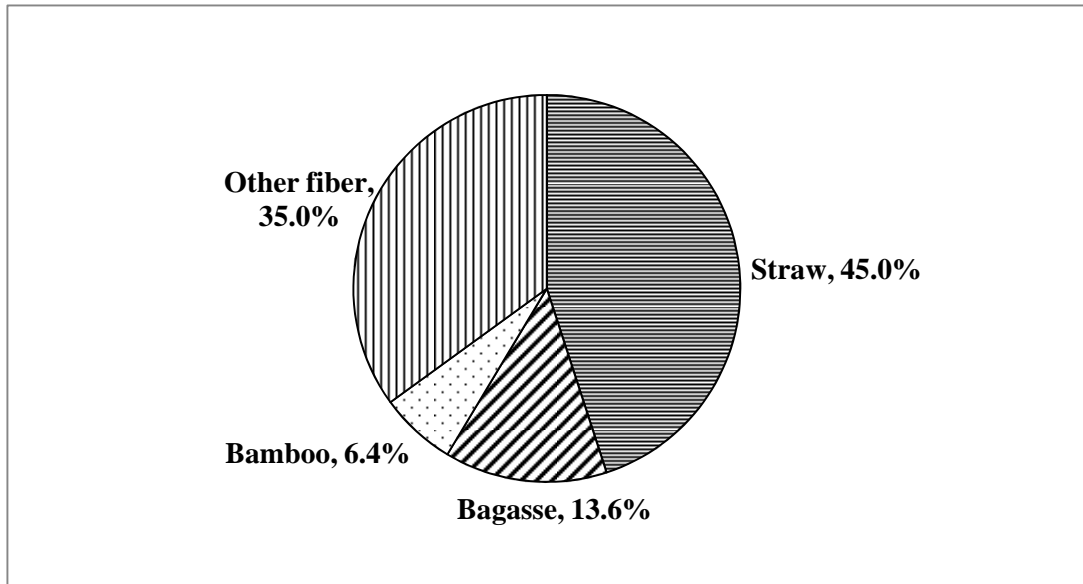


Figure 2.5: Raw material sources for non-wood pulp in 2002 (FAO)

The utilisation of non-wood plants for papermaking has some environmental advantages due to their relatively lower lignin content in comparison with wood. For instance, non-wood is basically easier to be delignified by pulping and bleaching processes and hence, allowing the production of full bleached pulp with less polluting process which associated with lesser amount of chemicals are consumed (Casey, 1980). In Western countries, non-wood pulp is more preferred to be used in the production of specialty paper. Flax, hemp and abaca are often used as reinforcement pulp to make very thin paper such as cigarette paper and bank notes, where good formation, strength and opacity are required (Sixta, 2006). Cotton fibre are relatively long and usually used as raw material for textile industry, but the cotton linter as well as those remaining fibres from textile cuttings are used for high quality writing and drawing papers (Pahkala, 2001). A part from that, agricultural residues are available in huge quantities at relatively a lower cost as they are co-product of the agricultural products which require no additional land for plantation (Rousu et al., 2002).

Nevertheless, the utilisation of non-wood also poses a lot of problems in the practice of pulp production. As show in Table 2.2, non-wood plants such as EFB, common reed, esparto, rice, oat and wheat straw contain high silica content, which can dissolve into the cooking liquor

during alkali pulping process and cause serious chemical recovery problems (Pahkala, 2001; Rousu et al., 2002). Furthermore, seasonality of annual crop gives difficulties in term of storing, harvesting, separating, drying, cleaning, handling and shipping. Since most of the non-wood plants are low bulk density, they face some transportation and storage problems (Ali et al., 2002; Rowell et al., 2000; Rousu et al., 2002).

Table 2.2: Silicate content of raw material

Raw material	Silicates (% on an oven-dry weight)
EFB (González et al., 2008)	2.3
Rice straw(González et al., 2008)	11.0
Kenaf (Khristova et al., 2002)	< 1.0
Oat straw (Pahkala, 2001)	4.0 - 7.0
Wheat straw (Pahkala, 2001)	3.0 - 7.0
Common reed (Pahkala, 2001)	2.0
Esparto (Pahkala, 2001)	2.0
Bamboo (Pahkala, 2001)	1.5 - 3.0
Bagasse (Pahkala, 2001)	0.7 - 3.0
Jute (Pahkala, 2001)	< 1.0
Coniferous trees (Pahkala, 2001)	< 1.0
Leaf trees (Pahkala, 2001)	< 1.0

## 2.2 Chemical composition and its effect on papermaking

Generally, lignocellulosic material from wood and non-wood plant consists of cellulose, hemicellulose, lignin, extractives and a minor part of inorganic matter. Cellulose is the predominant component which contributes 26-91% of the lignocellulosic material (Han, 1998). Thus it normally plays the important role in determining the suitability of the material to be used in papermaking. Basically, different types of raw materials compose different proportion of chemical composition which will influence their pulping and bleaching capability (Pahkala, 2001). Thus, many researches have been carried out extensively to understand the chemical composition in various raw materials as shown in Table 2.3.



Table 2.3: Chemical composition of non-woods and woods

Analysis (%)	Ash	Extractives			Lignin	Holo-cellulose	$\alpha$ - Cellulose	Hemi-cellulose*
		Alcohol-Benzene	1% NaOH	Hot-water				
EFB (Wanrosli et al., 2003)	5.4	2.3	N/a	N/a	17.2	82.5	60.6	21.9
Wheat straw (Deniz et al., 2004)	4.7	7.8	40.6	14.0	15.3	74.5	38.2	36.3
Cotton stalks (Ali et al., 2002)	1.8	2.9	39.6	10.8	22.5	N/a	48.8	N/a
Bagasse (Jahan et al., 2002)	1.8	8.0	41.0	12.9	17.8	49.4	N/a	N/a
Bamboo (Jahan et al., 2002)	2.5	6.2	27.3	9.4	28.0	75.5	N/a	N/a
Kenaf bast (Latifah et al., 2007)	6.4	2.1	28.4	5.5	14.3	80.0	54.5	25.5
Kenaf core (Latifah et al., 2007)	3.1	3.0	24.7	4.8	23.4	76.9	38.0	38.9
Rice straw (Rodríguez et al., 2008)	9.2	0.6	57.7	7.3	21.9	60.7	41.2	19.5
<i>Pine pinaster</i> (Rodríguez et al., 2008)	0.5	2.6	8.0	2.0	26.2	69.6	55.9	13.7
<i>Eucalyptus globulus</i> (Rodríguez et al., 2008)	0.6	1.2	12.4	2.8	20.0	80.5	52.8	27.7

Hemicellulose\* = (Holocellulose -  $\alpha$ -Cellulose)

### 2.2.1 Carbohydrates

The major carbohydrates portion of lignocellulosic material is composed of cellulose and hemicellulose with lesser amounts of starch and pectin. The combination of cellulose and the hemicellulose are generally known as holocellulose (Rowell et al., 2000, Rowell, 2005). Holocellulose is obtained by digesting the extractives free lignocellulosic sample with an acidified sodium chlorite to eliminate the residual lignin (Casey, 1980; Fengel and Wegener, 1989; Rowell et al., 2000). In general, the holocellulose consists mainly of basic sugars, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid and minor amounts of L-rhamnose and D-fucose. These sugar polymers are richer with hydroxyl groups which enable them to form hydrogen bonding fibres during the papermaking process (Rowell et al., 2000, Rowell, 2005).

Cellulose is a homopolysaccharide composed of D-glucose units which are linked together by (1→4)-glycosidic bonds and the degree of polymerization (DP) from 10,000 in native wood to 1,000 in bleached kraft pulp. Each of the cellulose molecules laterally exposes hydroxyl groups which are capable to form intra and intermolecular hydrogen bonds.

Bundles of cellulose molecules are arranged into ordered strands called fibrils, which are aggregated into structural fibrils which are highly crystalline. The presence of crystalline cellulose, with strong hydrogen bonds cellulose has a high tensile strength and is resistant to strong aqueous alkaline. The chemical attack can therefore be expected to occur primarily on amorphous cellulose, which has a lower packing density (Sjöström, 1993; Rowell et al., 2000; Pahkala, 2001; Rowell, 2005).

Unlike cellulose, which is a homopolysaccharide, hemicellulose is heteropolysaccharides. Hemicellulose has lower DP of 100-200 and is relatively easier to be hydrolyzed by chemical to their monomeric components containing mainly sugars D-xylopyranose, D-glucopyranose, D-galactopyranose, D-glucopyranosyluronic acid, D-mannopyranose and L-arabinofuranose with minor amounts of other sugars. In softwood, the main hemicellulose is galactoglucomannans, whereas in hardwood it is glucuronoxylan (Sjöström, 1993; Rowell et al., 2000; Pahkala, 2001; Rowell, 2005). On the other hand, similar to hardwood the hemicellulose of non-wood is normally composed of xylose unit. For instance, the hemicellulose from bamboo is built by a backbone polymer of D-xylopyranose with side chains of D-glucuronic acid, while in kenaf, it is also built by a backbone polymer of D-xylopyranose with side chains of D-galactose and L-arabinose (Rowell et al., 2000).

Referring to Table 2.3, EFB and kenaf bast have higher or comparable holocellulose content as compared to *Eucalyptus globulus* (hardwood), and much higher than *Pine pinaster* (softwood) and some of the non-wood plants. It is interesting to note that even though there is only a minor difference of holocellulose content between *Eucalyptus globulus*, EFB and kenaf bast, the  $\alpha$ -cellulose content of the EFB is about 10% higher than those of *Eucalyptus globulus* and kenaf bast. This indicates that the *Eucalyptus globulus* and kenaf bast basically contains higher hemicellulose content than EFB. In contrast, even though the holocellulose content of *Pine pinaster* is lower than some of the non-wood plants, it shows higher  $\alpha$ -

cellulose content. For example, non-wood plants of wheat straw (74.5%) and kenaf core (76.9%) have higher holocellulose content but lower in  $\alpha$ -cellulose content (38.2% vs 38%).

In papermaking, preserving the carbohydrate from serious degradation during pulping and bleaching processes is essentially an important factor because carbohydrate is the main contributing component to the pulp yield and the strength property of paper. Even though the presence of  $\alpha$ -cellulose content in raw material does not affect directly to pulping properties, the amount of the component basically may reflect the amount of pulp yield, where for a raw material with high amount of  $\alpha$ -cellulose, it may produce pulp in high yield (Shimada et al., 1988). For instance, kenaf bast with high  $\alpha$ -cellulose content (54.5%) imparts much higher soda-AQ pulp yield (54.1%) as compared to kenaf core (47.8%) with lower high  $\alpha$ -cellulose content (38%) (Khristova et al., 2002; Latifah et al., 2007). Thus, the high amount of  $\alpha$ -cellulose content present in the raw material is a great indicator of its potential as a papermaking raw material (Rodríguez et al. 2008). Besides, in papermaking, hemicellulose should also be retained as much as possible to preserve higher pulp yield and to get better paper property because the presence of hemicellulose will make it capable to improve interfibre bonding (Hocking, 2005).

### 2.2.2 Lignin

Lignin is polyphenolic, amorphous, three-dimensionally branched network polymer that plays an important mechanical support in plants. This structure serves as a binder in lignocellulosic plants that held together the fibres and stiffening agent within fibres. During chemical pulping, lignin is removed from the bundles fibre and allows the fibres to be separated easily. They are formed from three basic monomers and building units of all lignin as shown in figure 2.6 which are p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol.

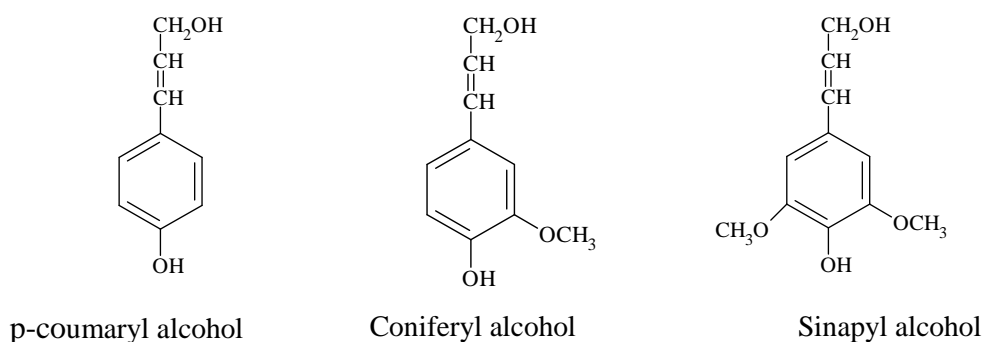


Figure 2.6: Chemical precursors of lignin (Britt, 1970; Fengel and Wegener, 1989; Lewin, 1991; Rowell et al., 2000)

Lignin structure and its amount exist variably among the major plant groups and among species (Pahkala, 2001). For example, hardwood lignin (guaiacyl-syringyl) is developed from coniferyl alcohol and sinapyl alcohol (3, 5-dimethoxy-4-hydroxycinnamyl alcohol) while softwood lignin (guaiacyl) is developed from coniferyl alcohol (3-methoxy-4-hydroxycinnamyl alcohol) (Browning, 1975; Lewin, 1991; Rowell et al., 2000). Generally, the amount of lignin present in softwood (26-32%) is invariably higher than those in hardwood (20-25%) (Sjöström, 1993). A part from that, lignin in some plants is formed from other than guaiacy and syringopropane units. For example, corn lignin consists of vanillin and syringaldehyde units along with substantial amounts of p-hydroxybenzaldehyde and bamboo lignin is formed from a mixture of dehydration polymer of coniferyl, sinapyl, and p-coumaryl alcohol (Rowell et al., 2000).

In plant's cell wall, the middle lamella and primary wall is often referred to as the compound middle lamella. This layer contains high lignin but it is thin, with only about 20-25% of the total lignin located in this layer (Sjöström, 1993). Thus, the rest of the lignin, about 75%, is located in the secondary cell wall since this layer accounts for most of the mass of the fibre (Lewin, 1991; Biermann, 1996; Rowell et al., 2000).

In the pulping process, the lignin of the raw material is considered as undesirable substance that creates most problems and should be removed during pulping or bleaching process

(Khristova et al., 1998; Wanrosli et al., 2007). Based on the published data shown in Table 2.3, wheat straw and kenaf bast show lowest lignin content compared to *Eucalyptus glubulus*, *Pine pinaster* and some of the non-wood plants. Meanwhile, the lignin content of the *Pine pinaster* is much higher than *Eucalyptus glubulus* and non-wood plants except for bamboo. The ease of delignification of the material during the chemical pulping process can be estimated from the amount of the lignin content; where for high lignin content, it requires high chemical consumption and or reaction time during pulping process (Ogunsile et al., 2006).

### 2.2.3 Extractive

#### 2.2.3 (a) Alcohol-benzene extractives

Extractive is the extraneous plant component that is generally present in small amounts and can be isolated by organic solvents or water. Extractive is a heterogenous group of compounds of lipophilic and hydrophilic including terpenes, fatty acids and its esters, tannins, volatile oils, polyhydric alcohols and aromatic compounds. The components of extractives are strongly dependent on the plant species, the position from heartwood to sapwood and the age of the tree (Browning, 1975; Higgins, 1977; Fengel and Wegener, 1989; Lewin, 1991; Rowell et al., 2000). Extractive often locates in the resin canals and the ray parenchyma cells. Besides, small amounts are also present in the middle lamellae, intercellulars and cell walls of tracheids and libriform fibres of plant (Fengel and Wegener, 1989).

Referring to Table 2.3, the organic solubility or known as extractive of wheat straw, bagasse and bamboo is significantly higher than those of *Eucalyptus globules*, *Pine pinaster* and the rest of non-wood plants. On the other hand, apart from rice straw, the extractive of *Eucalyptus globulus* is lower than those of *Pine pinaster* and non-wood plants. Since the *Eucalyptus globulus*'s extractive content is low, higher pulp quality is expected to be

obtained. This is because the presence of extractive components in the raw material causes pitch problems in the finishing of pulp and paper production and leads to important economic losses.

During alkaline pulping, most of the lipids from the fibres is removed and forms colloidal pitch, which can accumulate on the surface of pulp or certain part of machinery. Consequently, this reduces the quality of paper (Khristova and Karar, 1999; Gutiérrez et al., 2001). Moreover, some of the extractives can contribute to toxicity when they are released into effluents such as tannins, resin acids, stillbenes (Ali and Sreekrishnan, 2001). Besides, the presence of the extractives in high amount in the raw material will increase the consumptions of pulping chemical and also contribute to the increase of the viscosity of black liquor (Higgins, 1977). Thus, high extractive content is totally undesirable for papermaking as it may increase the pulping and bleaching burden (Ogunsile et al., 2006).

### 2.2.3 (b) 1% NaOH solubility

The purpose of this analysis is to determine the solubility of low-molecular-weight carbohydrate, mainly hemicellulose which is in close association with the cellulose in the cell wall of raw material (Khristova and Karar, 1999). Hemicellulose is usually branched and has much shorter molecular chains than cellulose which are easily dissolved and extractable from plants by weak alkali due to their amorphous structures and low molecular weights (Britt, 1970; Casey, 1980; Fengel and Wegener, 1989; Lewin, 1991).

As illustrated in Table 2.3, it is noted that the 1% NaOH solubility of *Pine pinaster* and *Eucalyptus globulus* are evidently lower than non-wood plants. The low value of 1% NaOH solubility observed in *Pine pinaster* and *Eucalyptus globulus* indicates less dissolution of cell wall materials when the wood chips are cooked with appropriate chemicals at elevated temperature and pressure.

### 2.2.3 (c) Hot water solubility

This determination is more probable to indicate the amounts of low molecular weight carbohydrates and phenolic substances (lignin, dyes, tannins, pectin substances) dissolving from the raw material. In general, the polyose group of galactans, especially arabinogalactans are water-soluble polysaccharides and are widely found in plants. During the chemical pulping, water-soluble arabinogalactans are relatively easy to be hydrolyzed to L-arabinose and D-galactose (Fengel and Wegener, 1989; Britt, 1970).

As similar to 1% NaOH solubility, the hot water solubility of *Pine pinaster* and *Eucalyptus globulus* are noticeably lower than non-wood plants as shown in Table 2.3. High hot water solubility is not desirable for the pulping process as it may attribute to the dissolution of the non fibrous substances and also some of the phenolic substances and causes massive loss of the pulp yield (Khristova et al. 1998; Jahan et al., 2007).

### 2.2.4 Inorganic content

The inorganic constituent of lignocellulosic material is usually referred to its ash content which is considered being the residue remaining after combustion of the organic matter at a temperature of  $525\pm 25^{\circ}\text{C}$  (TAPPI T211). The ash content consists mainly of various metal salts such as silicates, carbonates, oxalates and phosphates of potassium, magnesium, calcium, iron and manganese as well as silicon. Normally, they deposit in the cell walls, libriform fibres and lumina of parenchyma cells and also deposit in the resin canals and ray cells (Fengel and Wegener, 1989; Sjöström, 1993).

As shown in Table 2.3, woods, which is *Pine pinaster* and *Eucalyptus globulus* contains relatively lower ash content than non-wood plants. The low ash content of wood is a good indicator of its potential to be an excellent raw material for pulp and paper production. Generally, the ash content is contributed by inorganic content that affects the pulping

efficiency by increasing both the consumption of pulping chemicals and the burden of black liquor recovery system. Besides, it may affect the reaction of bleaching chemicals (hydrogen peroxide or ozone) toward the pulp during the bleaching process and thus have a negative effect in the pulp and paper brightness.

### 2.3 Kenaf

Kenaf is an annual plant and member of the *Hibiscus* family (*Hibiscus cannabinus L.*). It is a close relative of cotton and jute and has been cultivated in its native Africa since 4000 BC. Kenaf fibre offers the advantages of biodegradability and renewability, and is used in traditional products such as ropes, burlap, cordage and twine (Kaldor et al., 1990; Keshk et al., 2006; Moreau et al., 1995). Commercial use of kenaf in the United States begins in the 1940s when World War II interrupted Asian supplies of the jute fibre, which is used to produce cordage. In 1960, Agricultural Research Service (ARS) identified kenaf as the most promising fibre source for paper production among more than 500 species of the plants studied (Kugler, 1990; Sticker, 2006).

Kenaf has a high growth rate and reaches to a height of 5m to 6m with a diameter of 25-35 mm within five to six months (Kaldor, 1989; Kaldor et al., 1990; Zaveri, 2004). Study by USDA indicates that kenaf annually yields approximately 6 to 10 tons of dry fibre per acre, which is generally 3 to 5 times greater than the yield of Southern pine trees (Sabharwal et al., 1994). Kenaf grows well in many countries with a temperate or tropical climate and also on most land, except on land with gravelly and sandy soils. Besides, kenaf only requires few or no pesticides and fertilizer for its cultivation but it depends on the location it is grown (Liu, 2005; Zaveri, 2004).

Kenaf plant has a single, straight slender stalk without a branch. Kenaf consists of two distinct fibres, the outer fibrous bast and the inner woody core. The outer bast fibre and the



inner core fibre constitute about 35-40% and 60-65% respectively of the plant dry weight (Kaldor et al., 1990; Liu, 2005; Pande et al., 2000; Zaveri, 2004). In terms of physical property, the long bast fibre (3 to 4 mm) is comparable to softwood fibre, whereas the short core fibre (0.5 to 0.7 mm) is similar to hardwood fibre (Ahmed et al., 1998; Kaldor et al., 1990).

### 2.3.1 Factors effecting kenaf fibre's properties

Many studies have found that the chemical composition and physical properties of kenaf fibre can be affected by many factors such as cultivars of plant, different plantation year, growing condition, plantation soil, geographical location, different portion of the plant and the age of the plant harvested (Cook et al., 1998; Rowell and Stout, 1998; Rowell and Han, 1999; Rowell et al., 2000). Therefore, knowledge about the changes in both its chemical and physical properties of the plant is important to determine the suitable harvest time for processing industries, especially for the pulp and paper industry.

Rowell et al., (2000) found that the chemical composition of kenaf bast fibre has a close relationship with plant age. Based on their data, chemical composition of lignin, glucose and xylose contents are increased with increasing of plant age whereas arabinose and galactose contents are decreased as shown in Table 2.4. Besides, the changes of fibre physical properties on kenaf with plant age can also be seen from Table 2.5. It shows both the kenaf bast and core fibre's length, width and lumen width decreases with an increase of age. However, the cell wall thickness is not significantly affected by the difference of growing time (Rowell and Stout, 1998; Rowell et al., 2000).

Table 2.4: Changes in chemical composition of kenaf bast fibre with the growing time (Rowell et al., 2000)

DAP*	Chemical composition (Percent of oven dry basis)				
	Lignin	Glucose	Arabinose	Galactose	Xylose
42	6	33.2	3.18	0.62	7.31
57	8.32	35.5	2.21	0.55	8.08
77	9.23	40.5	2.05	0.39	9.16
161	10.2	39.2	2.54	0.56	9.75

\*Days after planting

Table 2.5: Changes in fibre physical properties of kenaf with the growing season (Rowell and Stout, 1998; Rowell et al., 2000)

Component	Stage of plant growth - Days after planting			
	90	120	150	180
<b>Bast fibre</b>				
Length (mm)	3.34	2.28	2.16	2.42
Width (microns)	18.3	14.5	13.6	15.1
Lumen Width (microns)	11.1	5.4	6.8	7.7
Cell wall thickness (microns)	3.6	4.6	3.4	3.7
<b>Core fibre</b>				
Length (mm)	0.55	0.54	0.45	0.36
Width (microns)	36.9	31.2	32	31.6
Lumen Width (microns)	22.7	14.8	18.6	18.7
Cell wall thickness (microns)	7.1	8.2	6.7	6.4

Furthermore, the chemical and physical properties in similar plant species also vary from plant to plant and within the different parts of the plant. Rowell et al., (2000) found that the chemical composition of kenaf varies in fibres from top to bottom of the plant. Data taken from the bottom of kenaf plant shows higher lignin, glucose and xylose contents while the top portion shows higher arabinose and galactose as shown in Table 2.6.

Table 2.6: Variations in chemical composition of kenaf between top and bottom portion (Rowell et al., 2000)

DAP*	Stalk portion	Chemical composition (Percent of oven dry basis)				
		Lignin	Glucose	Arabinose	Galactose	Xylose
42	Top	5.00	32.7	2.5	1.74	7.04
	Bottom	6.50	36	2.75	1.5	8.5
57	Top	5.10	30.6	3.11	1.96	6.87
	Bottom	9.00	38.2	2.49	1.47	8.93
77	Top	4.10	27.5	3.99	2.83	5.9
	Bottom	19.10	36.7	0.34	0.61	17.5

\*Days after planting

### 2.3.2 Production of pulp and paper from kenaf

Although kenaf was first introduced to the world in the 1940's during World War II, it was not ready to be commercialized. In 1986, due to the potential of kenaf as a sustainable solution for processing industries, the kenaf demonstration project is formed and as a cooperative effort between United States Department of Agricultural (USDA) and private company of kenaf international to commercialize kenaf for the manufacture of newsprint in United States (Kugler, 1996; Stricker, 2006). According to FAO (2003), kenaf is commercially and widely cultivated in more than 20 countries of the world, especially in India, China, Thailand and Vietnam (FAO, 2003). As reported by Han et al. (1997), the world's first commercial kenaf pulp mill, Phoenix Pulp & Paper Co. Ltd. located at Khon Kaen, Thailand is completed in 1982. This pulp mill is initially based on whole stalk kenaf with an annual production capacity of 70,000 t.

According to Myers and Bagby (1994), the earlier work on whole stalk kenaf is done for the production of linerboard grade chemi-thermo-mechanical pulp (CTMP). The study found that linerboards with acceptable strength can be made from blending 30-50% of the kenaf CTMP with loblolly pine kraft pulp. Besides, Myers and Bagby (1995) have also studied the

feasibility of using kenaf CTMP for printing and writing paper production. It is apparent from the study that the kenaf CTMP can be used by itself in printing and writing paper since its pulp quality is similar to aspen CTMP. Furthermore, Yang et al. (1996) has evaluated kenaf chemimechanical pulp (CMP) for offset newsprint. The study found that the resultant kenaf CMP newsprint has a higher inking efficiency than the wood newsprint.

A relatively new developed chemimechanical pulping process-alkaline peroxide mechanical pulping (APMP) of kenaf and straw has been carried out by Xu (2000), and he found that both the APMP pulp appear to be about the same in strength properties as compared to aspen APMP pulp. In addition, the study also demonstrates that the kenaf fibre is relatively easy to be bleached and its resultant pulp also impart higher tensile strength at a given density in comparison to straw APMP as well as aspen APMP pulp. Thus, the author suggests that kenaf APMP pulp exhibit a good potential to be used for applications similar to aspen APMP pulp or market bleached chemithermomechanical pulp (BCTMP), which are normally used for printing or writing paper, tissue and high brightness paperboard grade. Besides, Xu (2001) also commented that the kenaf APMP pulp has higher intrinsic pulp strength and light scattering properties than bagasse APMP pulp.

For the newsprint production, besides the earlier attempt done by Yang et al. (1996), the work is continued by Mohta et al. (2004) through the production of kenaf refiner mechanical pulp (RMP). The study reported that the resultant kenaf RMP is not only very suitable for the production of newsprint but it is capable of enhancing various mechanical properties through blending 20-30% of the bleached kenaf RMP with deinked recycled newsprint.

The utilisation of whole stalk kenaf in the production of chemimechanical and mechanical pulp has given good results as mentioned earlier. However, many researchers also suggested that the kenaf bast and core should be separated prior to the pulping process since they differ greatly in both the fibre physical and chemical properties, which will cause different pulping

and papermaking characteristics (Kaldor, 1989; Pande, 1999). It is expected that better pulping results can be obtained by processing the bast and core fibre separately. Nevertheless, owing to the difficulties in preparing the separated kenaf bast and core fibres on a scale commensurate with the demands of a pulp mill, the commercial pulping of kenaf is normally directed towards whole stalk pulping, although the fibre separation process's procedures have been developed and patented by Ankal Pty. Ltd., Australia in 1974 (Kaldor, 1989; Kaldor et al., 1990).

Regardless the difficulties of separating the bast and core fibres, some researches based on the separated fibres have also been carried out in the late 1990s. According to the work done by Han et al. (1997), the authors have verified that the minimum kraft pulping condition to fully cook both the kenaf bast and core is at 16% NaOH, 20% Na<sub>2</sub>S and cooks for 0.5 hour at 170°C. Moreover, Han (1999) has pointed out that the kenaf bast can be cooked well by soda-AQ pulping with only 12% active alkali (AA) and 0.15% AQ, cooks for 2 hours at 160°C. On the other hand, the study also found that this condition is insufficient to cook the kenaf core fibre since the resultant pulp contains bundles of fibre, which are actually uncooked. Thus, a higher alkali charge should be employed in order to fully cook the core fibre, which contains higher lignin content. Their results show that the minimum soda-AQ pulping condition to fully cook the kenaf core is 15% AA, 0.15% AQ and cooks for 2 hours at 160°C. In comparison between kraft and soda-AQ pulp, both the yield and strength properties of the paper produced are comparable. Thus, Han (1999) concluded that soda-AQ pulping is more favourable than kraft pulping for kenaf. Moreover, soda-AQ pulping also shows lower environmental impact as compared to kraft pulping.

On the other hand, a study of the effects of soda, soda-AQ, alkaline sulphite-anthraquinone (AS-AQ) and alkaline sulfite-anthraquinone-methonol (ASAM) pulping on kenaf bast, core and whole stalk is also carried out under different conditions by Khritova et al. (2002). The author commented that among the four pulping methods, the AS-AQ method is particularly

not well suited for kenaf core since it yield pulp with higher kappa number, which is double to those pulp from other methods, even though the given data shows that the kenaf core imparts higher or comparable strength properties as compared to those of soda, soda-AQ and ASAM.

Generally, the selection of the pulping process depends on the functions of the end-use product. It is well known that the usage and the potential application of the kenaf bast and core are greatly different from each other. For example, kenaf bast fibre has superior fibre length and naturally low lignin content; therefore it is more favourable to be processed into speciality papers such as high quality stationery or filter paper (Khristova et al., 1998; Webber and Bledsoe, 2002; Webber et al., 2002). Therefore, in order to make use of such a quality material, chemical pulping process viz kraft, kraft-AQ, soda, soda-AQ and neutral sulphite are more favourable (Khristova et al., 2002).

On the other hand, kenaf core is less suitable to be cooked by chemical pulping because it is relatively more difficult to be cooked as compared to kenaf bast, which gives higher kappa number and lower pulp yield (Khristove et al. 2002). Although the separated kenaf core alone actually is seldom used for pulp and paper production, the mirco-porous structures of kenaf core make it more useful for absorbent application as it has high absorbency property. To further enhance the absorbency property, the kenaf core is more favourably treated by mechanical pulping process, where the mechanical refining action may increase the surface area of fibre and subsequently enhance fibre tendency to form a large amount of capillaries (Zaveri, 2004). Therefore, it is likely that it will be used as absorbent applications such as bedding in horse stables, poultry litter, a filter medium for fruit juices and engine oil and as a medium for oil spill cleanup (Bel-Berger et al., 1999; Webber and Bledsoe, 2002; Liu, 2005).