

**CLEAN FRACTIONATION OF BIOMASS - STEAM EXPLOSION AND
EXTRACTION**

Mazlan Ibrahim

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
in
Forest Products

Wolfgang G. Glasser, Chair
Foster A. Agblevor
Richard F. Helm

February 24, 1998
Blacksburg, Virginia

Keywords: Red oak (*Quercus rubra*), Oil palm (*Elaeis guineensis*), Hydrothermal process, Cellulose, Lignin, Hemicelluloses, Summative analysis.

CLEAN FRACTIONATION OF BIOMASS - STEAM EXPLOSION AND EXTRACTION

Mazlan Ibrahim

(ABSTRACT)

The fractionation of two biomass resources, red oak (*Quercus rubra*) chips and oil palm (*Elaeis guineensis*) trunk solids, into constitutive chemical components, cellulose, hemicelluloses (called “other carbohydrates”) and non-carbohydrates (includes lignin, tannins, etc.), was studied quantitatively in terms of relative cleanness. Red oak chips were steam exploded using a batch reactor at five different treatment severities, R_o 5,000, 10,000, 15,000, 20,000 and 35,000. Steam exploded fibers (SEF) of each severity were extracted with water and alkali.

Mass fractionation and summative analysis data of all solid biomass fractions were determined. These data were interpreted in term of a unifying clean fractionation concept designed to evaluate the effectiveness of the fractionation processes. Within a series of severities applied to a single biomass resource, the quantitative clean fractionation can be used to choose an optimum severity for the isolation of any particular component fraction.

The red oak results revealed that 25 % (on average) of biomass solids were lost during steam explosion. Cellulose remained almost unaffected (retained in fibers form) by water and alkali extraction. About 35-55 % of the hemicelluloses can be recovered in the water extracted liquor fraction (WEL). The remaining non-cellulosic carbohydrates were lost during steam explosion, especially at high severity. At R_o 10,000 and above, alkali extracted fibers (AEF) consists almost entirely of cellulose and non-carbohydrates. The majority of the non-carbohydrates component (> 50 %) can be isolated by alkali extraction. The non-carbohydrate component harvested increased with severity to 67 % at R_o 35,000

The optimum severity to recover the other carbohydrates component in the WEL solids and to obtain the highest yield of the AEF solids free of hemicelluloses was somewhere between at R_0 10,000 to 15,000. The best severity to recover non-carbohydrates from WEF was at R_0 35,000.

Oil palm trunk solids were fractionated in a likewise manner. However, since oil palm biomass contains significant quantities of starch, the fractionation protocol was complicated by analytical uncertainties. It appeared that other carbohydrates required severities above R_0 2,000 to be released into the aqueous extract. A significant portion (> 50 %) of the non-carbohydrates component becomes alkali soluble when severity is above R_0 8,000.

ACKNOWLEDGEMENTS

The author expresses his gratitude to his advisor, Professor Wolfgang G. Glasser, for his encouragement and support in pursuing his graduate program, and his guidance in thesis research.

He also thanks Professors Richard F. Helm and Foster A. Agblevor for serving on his graduate committee. He is very grateful to Dr. Rajesh K. Jain, Mr. Robert S. Wright and Mrs. Jody Jervis for their assistance and guidance in the course of completing this work. The author also thanks to the Universiti Sains Malaysia for its financial support.

Finally, the author expresses his thanks to his loving wife, Zahanim Zakaria and his daughter, Nadhrah Mazlan for their moral and personal support.

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
ACKNOWLEDGMENTS.....	iv
TABLE OF CONTENTS	v
LIST OF FIGURES.....	viii
LIST OF TABLES.....	x
ABBREVIATIONS	xii
1.0 INTRODUCTION	1
2.0 LITERATURE REVIEW.....	3
2.1 Lignocellulosic Biomass Materials	3
2.2 Lignocellulose Structure	3
2.2.1 Cell Wall Structure	3
2.2.2 Chemical Structure.....	7
2.2.2.1 Cellulose.....	7
2.2.2.2 Hemicelluloses and Starch.....	12
2.2.2.3 Lignin	16
2.2.2.4 Extractives.....	16
2.3 Steam Explosion.....	19
2.4 Fractionation	20
3.0 MATERIALS AND METHODS.....	22
3.1 Materials	22
3.1.1 Starting Material for Steam Explosion	22
3.1.2 Materials for Extractions	22
3.1.3 Materials for Chemical Analysis.....	22
3.2 Methods	23
3.2.1 Steam Explosion	23
3.2.2 Extractions.....	26
3.2.2.1 Water Extraction.....	26
3.2.2.2 Alkali Extraction.....	28
3.2.2.3 Acetic Acid Extraction.....	28
3.2.2.4 Ethanol Extraction	30

3.2.3	<i>Chemical Analysis (Summative Analysis)</i>	32
3.2.3.1	Acid hydrolysis	32
3.2.3.2	Non-Carbohydrates (Lignin and Tannins)	33
3.2.3.2.1	<i>Klason Lignin (Including Tannins)</i>	33
3.2.3.2.2	<i>Acid Soluble Lignin (Including Tannins)</i>	33
3.2.3.3	Carbohydrates.....	34
3.2.3.3.1	<i>Furaldehyde(s)</i>	34
3.2.3.3.2	<i>Sugars</i>	34
4.0	DATA INTERPRETATION	37
4.1	Mass Fraction	37
4.1.1	<i>Steam Explosion</i>	37
4.1.1.1	Starting Material (SM).....	39
4.1.1.2	Steam Exploded Fibers (SEF)	39
4.1.1.3	Loss.....	40
4.1.2	<i>Water Extraction</i>	40
4.1.2.1	Water Extracted Fibers (WEF).....	40
4.1.2.2	Water Extracted Liquor (WEL).....	42
4.1.3	<i>Alkali Extraction</i>	42
4.1.3.1	Alkali Extracted Fibers (AEF).....	42
4.1.3.2	Alkali Extracted Liquor (AEL).....	44
4.1.4	<i>Acetic Acid and Ethanol Extractions</i>	45
4.2	Chemical Composition (i.e., Summative Analysis)	45
4.2.1	<i>Non-Carbohydrates (i.e., Lignin and Tannins)</i>	46
4.2.2	<i>Cellulose</i>	50
4.2.3	<i>Other Carbohydrates</i>	51
4.2.4	<i>Unknowns</i>	52
4.3	Combination of Mass Fractionation and Summative Analysis Data 56	
4.3.1	<i>Starting Material (SM)</i>	56
4.3.2	<i>Water Extracted Liquor (WEL)</i>	56
4.3.3	<i>Alkali Extracted Fibers (AEF)</i>	57
4.3.4	<i>Water Extracted Fibers (WEF)</i>	57
4.3.5	<i>Alkali Extracted Liquor (AEL)</i>	63
4.3.6	<i>Loss</i>	63
4.3.7	<i>Outcomes Assessment of Mass Fractionation and Summative Analysis</i>	63
4.4	Clean Fractionation	67
5.0	RESULTS AND DISCUSSION	72
5.1	Clean Fractionation of Red Oak (<i>Quercus rubra</i>)	72
5.1.1	<i>Mass Fraction Flow</i>	72
5.1.2	<i>Summative Analysis - Starting Material</i>	73
5.1.3	<i>Summative Analysis</i>	75

5.1.4	<i>Fractionation Assessment</i>	78
5.1.5	<i>Clean Fractionation Concept</i>	81
5.1.5.1	Ideal Case	81
5.1.5.2	Series of Severity	84
5.2	Clean Fractionation of Oil Palm Trunk Solids	97
5.2.1	<i>Oil Palm Trunk Solids</i>	97
5.2.2	<i>Mass Fraction Flow</i>	97
5.2.3	<i>Summative Analysis</i>	97
5.2.4	<i>Fractionation Assessment</i>	102
5.2.5	<i>Clean Fractionation Concept</i>	102
6.0	CONCLUSIONS AND RECOMMENDATIONS	111
	REFERENCES	112
	VITA	115

LIST OF FIGURES

		Page
Figure 1	Schematic illustration of the cell wall of wood cells which generally applies to many cells in both softwoods and hardwoods	4
Figure 2	Schematic illustration of the layers of wood fibers	5
Figure 3	Schematic illustration of the relative thickness of cell wall layers for wood fibers.....	6
Figure 4	Schematic illustration of the cellulose chain.....	11
Figure 5	Schematic illustration of sugar units of hemicelluloses	13
Figure 6	Schematic illustration of xylans. A - Partial xylan structure from hardwood chain. B - Partial xylan structure from softwood chain	14
Figure 7	Schematic illustration of starch. A - Amylose chain. B - Amylopectin chain	15
Figure 8	Schematic illustration of building units of lignin.....	17
Figure 9	Schematic illustration of tannins in red oak. A - Hydrolysis products of hydrolyzable tannins. B - Flavonoid molecules, members of the class of condensed tannins	18
Figure 10	Schematic illustration of the batch steam explosion unit at T. M. Brooks Forest Products Center of Virginia Tech.....	25
Figure 11	Schematic illustration of water, alkali and acetic acid extractions apparatus	29
Figure 12	Schematic illustration of the Parr reactor used for ethanol extraction...	31
Figure 13	Schematic illustration of the ion exchange bed set-up used for sugar analysis.....	36
Figure 14	Schematic biomass fractionation diagram	38
Figure 15	Schematic flow chart of the acid hydrolysis (AH) and the constituent analysis of the acid hydrolyzate used for determining the chemical composition of biomass fractions	48
Figure 16	Schematic illustration of the data interpretation protocol: non-carbohydrates, cellulose and other carbohydrates are the components determined directly from experimental data.....	49

Figure 17	Schematic mass fraction and chemical composition flow chart including experimental and calculation data.....	55
Figure 18	Schematic presentation of chemical composition, mass fraction and normalized chemical composition data for the case of the WEL fraction.....	60
Figure 19	Plot of the clean fractionation for red oak at R_o 15,000.....	69
Figure 20	Plot of the clean fractionation scheme - ideal case scenario.....	83
Figure 21	Plot of the clean fractionation scheme - red oak at R_o 5,000.	85
Figure 22	Plot of the clean fractionation scheme - red oak at R_o 10,000.	86
Figure 23	Plot of the clean fractionation scheme - red oak at R_o 15,000	87
Figure 24	Plot of the clean fractionation scheme - red oak at R_o 20,000	88
Figure 25	Plot of the clean fractionation scheme - red oak at R_o 35,000	89
Figure 26	Plot of the clean fractionation scheme - red oak at R_o 35,000 (acetic acid).....	90
Figure 27	Plot of the clean fractionation scheme - red oak at R_o 35,000 (ethanol).....	91
Figure 28	Relationship between maximum slope parameter and severity of red oak for cellulose, non-carbohydrates and hemicelluloses (i.e., other carbohydrates) isolation.....	96
Figure 29	Plot of the clean fractionation scheme - oil palm trunk solids at R_o 600	106
Figure 30	Plot of the clean fractionation scheme - oil palm trunk solids at R_o 2,000	107
Figure 31	Plot of the clean fractionation scheme - oil palm trunk solids at R_o 10,000.....	108
Figure 32	Relationship between maximum slope parameter and severity of oil palm trunk solids for cellulose, non-carbohydrates and hemicelluloses (i.e., other carbohydrates) isolation	110

LIST OF TABLES

	Page
Table 1 Average chemical composition of softwoods, hardwoods and wheat straw	8
Table 2. Chemical composition of red oak (<i>Quercus rubra</i>)	9
Table 3 Cellulose content of various lignocellulosic materials	10
Table 4 Steam explosion conditions of red oak.....	24
Table 5 Sample designation of fibers processed by steam explosion and post treatment	27
Table 6 Mass fraction data of red oak at R _o 15,000	53
Table 7 Chemical composition of red oak at R _o 15,000	54
Table 8 Chemical composition of starting material (SM)	58
Table 9 Normalized chemical composition of WEL	59
Table 10 Normalized chemical composition of AEF	61
Table 11 Normalized chemical composition of WEF	62
Table 12 Normalized chemical composition of AEL.....	64
Table 13 Normalized chemical composition of Loss	65
Table 14 Outcomes assessment of mass fractionation and summative analysis of red oak at R _o 15,000.....	66
Table 15 Clean fractionation of red oak at R _o 15,000	68
Table 16 Clean fractionation slope parameters at R _o 15,000	71
Table 17 Mass fractionation data of red oak.....	74
Table 18 Analysis data of red oak fractions	76
Table 19 Chemical composition of red oak fractions	77
Table 20 Outcomes assessment of mass fractionation and summative analysis data of red oak.....	79
Table 21 Mass retention of solid fiber fractions by stage (ideal case and red oak) 82	82
Table 22 Comparison of clean fractionation slope parameters of red oak.....	92

Table 23	Comparison of lignin extraction data (red oak, R _o 35,000).....	95
Table 24	Mass fractionation data of oil palm trunk solids	99
Table 25	Analysis data of oil palm trunk solids fractions.....	100
Table 26	Chemical composition of oil palm trunk solids fractions.....	101
Table 27	Outcomes assessment of mass fractionation and summative analysis data of oil palm trunk solids	104
Table 28	Mass retention of solid fiber fractions of oil palm trunk. solids.....	105
Table 29	Comparison of clean fractionation slope parameters of oil palm trunk solids.....	109

ABBREVIATIONS

AcEF	Acetic acid extracted fibers
AcEL	Acetic acid extracted liquor
AEF	Alkali extracted fibers
AEL	Alkali extracted liquor
AH	Acid hydrolysis
AIL	Acid insoluble lignin/tannins
ASL	Acid soluble lignin/tannins
CC	Chemical composition
EtEF	Ethanol extracted fibers
EtEL	Ethanol extracted liquor
2-F	2-furaldehyde
HMF	5-(hydroxymethyl)-2-furaldehyde
HPLC	High performance liquid chromatography
MF	Mass fraction
OPT	Oil palm trunk solids
SEF	Steam exploded fibers
SM	Starting material
WEF	Water extracted fibers
WEL	Water extracted liquor