CHAPTER 5

5.0 RESULTS AND DISCUSSION

5.1 Clean Fractionation of Red Oak (*Quercus rubra*)

5.1.1 *Mass Fraction Flow*

Mass fraction flow refers to the flow of processed biomass from the beginning of steam explosion to the end of extractions. Mass fractions are determined based on the dry weight of starting material (SM). SM is chosen as a reference because it represents the initial mass of the fractionation. After each fractionation step (steam explosion, water extraction, alkali extraction, acetic acid extraction, or ethanol extraction), the mass of the resulting fraction is always less than SM. Therefore, SM is a suitable reference point to use as a basis for mass comparison in order to measure the effectiveness of the fractionation on each step. In addition, mass fractionation always refers to percentage on dry weight basis because of its stability and constancy.

Red oak chips as SM were separated into SEF and Loss fractions by steam explosion. SEF was segregated into WEF (solids fraction) and WEL (soluble fraction) by water washing; and WEF was separated into AEF or AcEF or EtEF (solids fractions) and AEL or AcEL or EtEL (soluble fractions) by lignin extracting with alkali or acetic acid or ethanol (Figure 17).

Mass losses during steam explosion are instrumentally unavoidable. Fibers and/or volatile substances (furaldehyde(s), acetic acid and steam volatile extractives) can be lost through the venting of the cyclone, adherence to the cyclone and pipeline walls, splashing and wash out during cleaning of the instrument. Therefore, mass fraction of Loss can only be calculated by difference (by subtracting mass fraction of SEF from SM). This Loss fraction is greatest for single batch explosion experiments under high severe conditions, and it can be minimized by multiple replications that avoid system clean up between batches. Mass fractions of solid fractions (WEF, AEF, AcEF and EtEF) are determined directly from their weight and mass fractions of soluble fractions (WEL, AEL, AcEL and EtEL) are calculated by difference.

The mass fractions of different severity of red oak are listed in Table 17. Based on these results, the SEF fraction represents approximately 75 % of SM (total wood weight). However, at lowest severity (R_o 5,000), the mass fraction of SEF is higher (i.e. less losses). This is due to the lowest pressure/temperature and not much mass loss during the explosion (lowest Loss fraction within the severity series). WEF and AEF reach a minimum at R_o 20,000 and the AEL fraction is highest at both lowest and highest severity. Extraction with acetic acid and ethanol produced slightly higher delignification fiber solids yield than alkali. The ethanol extraction result is agrees with earlier result obtained by Wallis and Wearne.[42]

5.1.2 *Summative Analysis - Starting Material*

The chemical composition of red oak (*Quercus rubra*) chips from this experiment is determined as follows; 35.46 % cellulose, 18.76 % other carbohydrates, 28.95 % non-carbohydrates and 16.83 % unknowns. The content of cellulose and hemicelluloses (other carbohydrates) are below the average for typical hardwoods and red oak data (Tables 1 and 2). In contrast, the content of non-carbohydrates (lignin and tannins) corresponds to the sum of Klason lignin and extractives according to Pettersen [36] . The unknowns obviously contain degradation products from the carbohydrate components that have escaped analytical detection.

Table 17. Mass fractionation data of red oak.

Treatment condition	Mass fraction, % of SM									
	SEF	Loss[1)]	WEF	WEL[1)]	AEF	AEL[1)]	AcEF	AcEL[1)]	EtEF	EtEL[1)]
R_o 5,000	83.1	16.9	66.0	17.1	43.4	22.6	-	-	-	-
R_o 10,000	77.4	22.6	56.3	21.1	38.1	18.2	-	-	-	-
R_o 15,000	74.2	25.8	53.9	20.3	35.5	18.4	-	-	-	-
R_o 20,000	75.4	24.6	52.9	22.5	34.8	18.1	-	-	-	-
R_o 35,000 [2)]	75.6	24.4	61.2	14.4	39.3	21.9	43.7	17.5	42.9	18.3

1) Calculated by difference.

2) Data adjusted to reflect losses typically encountered during single batch experiments; average loss-figures were lower for the lowest-severity batch (i.e., R_o 5,000) as well as for the R_o 35,000-batch (i.e., 18 %) owing to mildness of conditions and 12-fold replication, respectively.

5.1.3 *Summative Analysis*

Some biomass fractions were subjected to the summative analysis protocol to determine their chemical composition. The chemical analysis was conducted by standard hydrolysis with 72 % sulfuric acid and either gravimetric, spectrophotometric, or chromatographic detection of the hydrolyzed products.

The analytical protocol which was adopted from work by Kaar et al. [23, 24], yielded quantitative information on the content of non-carbohydrates (lignin and tannins); cellulose content (which was taken as the only component containing glucose); content of other carbohydrates (representing branched heteropolysaccharides, also called hemicelluloses or polyoses and assumed to contain all identified sugars other than glucose); and the content of a component of unknowns. The unknowns, which are determined by difference, represent such volatiles as acetic acid and such unidentified sugar degradation products as sugar acids. Whereas, the quantitative identification of unknowns is technically feasible, their overall low yield made their individual quantitative determination impractical.

Analysis results obtained from experiments with individual WEF, WEL, AEF, AcEF and EtEF are presented in Table 18. Furaldehyde(s) content averaged 10 % of pentoses. The amount of 2-F was always higher than HMF in WEL fractions but in other fractions (WEF, AEF, AcEF and EtEF), the amount of HMF was about double that of 2-F. The monosacharide mixture becames progressively more dominated by glucose as extraction proceeded. Only WEL showed a high content of xylose (30-40 %) and detectable amounts of galactose, arabinose and mannose components in the fractions.

Data from Table 19 suggest that non-carbohydrates varied between 10-40 % of the biomass fractions. Among the solid fibers, WEF had the highest amount of non-carbohydrates (30-40 %). Non-carbohydrate content of AEF fractions was reduced by about 50-70 % from the WEF fractions by alkali extraction. Within the WEF and WEL fractions from different severity, non-carbohydrates increased with increasing severity.

Table 18. Analysis data of red oak fractions.

Biomass fraction	Chemical composition, % of biomass fraction [1)]								
	AIL [2)]	ASL [3)]	2-F [4)]	HMF [5)]	Glu [6)]	Xyl [7)]	Gal [8)]	Ara [9)]	Man [10)]
SM [11)]	23.61	5.34	1.11	0.93	37.88	16.11	2.25	1.17	0.00
WEF-5	30.38	1.98	0.38	0.41	50.32	6.05	0.00	0.00	1.78
WEF-10	33.07	1.91	0.23	0.42	49.47	3.20	0.00	0.00	0.00
WEF-15	35.91	2.17	0.22	0.44	50.09	2.89	0.00	0.00	0.00
WEF-20	35.62	1.92	0.19	0.43	51.90	2.74	0.00	0.00	0.00
WEF-35	36.87	2.08	0.20	0.40	48.65	2.87	0.00	0.00	0.00
WEL-5	5.16	6.04	3.97	0.72	3.72	41.98	5.45	2.08	2.11
WEL-10	7.45	5.81	2.92	0.19	4.34	40.65	4.97	1.92	3.83
WEL-15	9.98	6.51	2.92	0.20	4.52	38.71	4.98	1.83	4.06
WEL-20	11.76	6.06	2.94	0.17	4.76	33.01	4.51	1.55	3.62
WEL-35	12.14	7.85	2.94	0.30	7.74	30.03	4.85	1.54	5.85
AEF-5	14.64	1.25	0.33	0.59	68.36	4.99	0.00	0.00	0.00
AEF-10	10.43	0.79	0.23	0.62	76.08	4.38	0.00	0.00	0.00
AEF-15	11.04	0.79	0.20	0.65	76.76	3.14	0.00	0.00	0.00
AEF-20	13.59	0.82	0.22	0.66	75.34	2.84	0.00	0.00	0.00
AEF-35	10.52	0.89	0.26	0.62	74.03	3.99	0.00	0.00	0.00
AcEF-35	19.24	0.71	0.22	0.58	68.00	3.15	0.00	0.00	0.00
EtEF-35	18.33	1.06	0.23	0.55	68.27	4.16	0.00	0.00	0.00

1) Data are obtained by single determination
2) Acid insoluble lignin/tannins
3) Acid soluble lignin/tannins
4) 2-furaldehyde
5) 5-(hydroxymethyl)-2-furaldehyde
6) Glucose
7) Xylose
8) Galactose
9) Arabinose
10) Mannose
11) Starting material, red oak chips

Table 19. Chemical composition of red oak fractions.

Biomass fraction	Chemical composition, % of biomass fraction			
	Cellulose	Other carbohydrates	Non-carbohydrates	Unknowns [1)]
SM	35.46	18.76	28.95	16.83
WEF-5	45.89	7.46	32.36	14.29
WEF-10	45.14	3.14	34.98	16.74
WEF-15	45.73	2.84	38.08	13.35
WEF-20	47.34	2.67	37.54	12.45
WEF-35	44.37	2.79	38.95	13.89
WEL-5	4.41	51.05	11.21	33.33
WEL-10	4.19	49.40	13.26	33.15
WEL-15	4.35	47.82	16.49	31.34
WEL-20	4.53	41.77	17.83	35.87
WEL-35	7.41	41.45	19.99	31.15
AEF-5	62.39	4.85	15.89	16.87
AEF-10	69.38	4.17	11.22	15.23
AEF-15	70.05	3.04	11.84	15.07
AEF-20	68.77	2.80	14.41	14.02
AEF-35	67.54	3.87	11.41	17.18
AcEF-35	62.25	3.97	19.39	14.39
EtEF-35	62.05	3.08	19.95	14.92
AEL-5 [1)]	14.22	12.47	63.97	9.34
AEL-10 [1)]	-5.41	0.99	84.53	19.89
AEL-15 [1)]	-0.95	2.46	88.44	10.05
AEL-20 [1)]	5.98	2.42	82.18	9.42
AEL-35 [1)]	2.95	0.86	88.19	8.01
AcEL-35 [1)]	-0.26	-0.16	87.78	12.64
EtEL-35 [1)]	3.13	2.11	83.27	11.49
Loss-5 [1)]	26.16	30.19	33.54	10.11
Loss-10 [1)]	40.55	29.07	28.58	1.80
Loss-15 [1)]	38.46	29.18	19.66	12.69
Loss-20 [1)]	38.23	32.26	20.68	8.83
Loss-35 [1)]	29.68	45.46	9.12	15.74

1) Calculated by difference

Within the limits of the unaccounted for losses from the mass fractionation flow and the unknown chemical components escaping quantitative detection, the analytical results can be summarized in terms of the composition of the biomass fractions in terms of cellulose content, other carbohydrate content, non-carbohydrates content and unknowns (Table 19).

Cellulose contents are highest in WEF, AEF, AcEF and EtEF fractions (45-70 %) and other carbohydrates are dominant in WEL fraction. Based on calculation (by difference), unknowns range from 10-35 %. AEL, AcEL and EtEL fractions are rich in non-carbohydrates. In Loss fraction, the data reveals that cellulose, other carbohydrates and non-carbohydrates are evenly distribute to 30 % on average.

5.1.4 *Fractionation Assessment*

By combining mass fractionation data with analysis results describing the chemical composition of individual fractions, a quantitative fractionation assessment can be conducted that accounts for the quality of the fractionation, or the cleanness of the fractionation process and its products. The determination of chemical components of each biomass fraction (Table 19) involves the quantitation of cellulose, other carbohydrates, non-carbohydrates, and unknowns for the WEL, AEL, AEF, and Loss fraction. Total mass fraction data must correspond to the mass balance data; and total chemical component analysis must correspond to the fractional component analysis conducted on the starting material (red oak chips). Because certain figures are derived by difference, negative numbers may occur which define the limits of accuracy of the method chosen. The results for all isolated fractions are summarized in Table 20. By using SM as reference, total of mass balance (WEL + WEF + Loss or WEL + AEL + AEF + Loss) and total of chemical composition (cellulose + other carbohydrates + non-carbohydrates + unknowns) for each severity is 100 %.

Table 20. Outcomes assessment of mass fractionation and summative analysis data of red oak.

Treatment condition	Chemical component	Mass fraction, % of SM 1)					Total, % of SM
		WEL	WEF	AEL 2)	AEF	Loss 3)	
R_o 5,000	Cellulose	0.8	30.2	3.2	27.0	4.4	35.4
	Other carbohydrates	8.7	4.9	2.8	2.1	5.1	18.7
	Non-carbohydrates	1.9	21.4	14.5	6.9	5.7	29.0
	Unknowns	5.7	9.5	2.1	7.4	1.7	16.9
	Total, % of SM	17.1	66.0	22.6	43.4	16.9	100.0
R_o 10,000	Cellulose	0.9	25.4	-1.0	26.4	9.2	35.5
	Other carbohydrates	10.4	1.8	0.2	1.6	6.6	18.8
	Non-carbohydrates	2.8	19.7	15.4	4.3	6.4	28.9
	Unknowns	7.0	9.4	3.6	5.8	0.4	16.8
	Total, % of SM	21.1	56.3	18.2	38.1	22.6	100.0
R_o 15,000	Cellulose	0.9	24.7	-0.2	24.9	9.9	35.5
	Other carbohydrates	9.7	1.5	0.4	1.1	7.5	18.7
	Non-carbohydrates	3.3	20.5	16.3	4.2	5.1	28.9
	Unknowns	6.4	7.2	1.9	5.3	3.3	16.9
	Total, % of SM	20.3	53.9	18.4	35.5	25.8	100.0
R_o 20,000	Cellulose	1.0	25.0	1.1	23.9	9.4	35.4
	Other carbohydrates	9.4	1.5	0.5	1.0	7.9	18.8
	Non-carbohydrates	4.0	19.8	14.8	5.0	5.1	28.9
	Unknowns	8.1	6.6	1.7	4.9	2.2	16.9
	Total, % of SM	22.5	52.9	18.1	34.8	24.6	100.0

Table 20. Continued from previous page.

Treatment Condition	Chemical Component	Mass Fraction, % of SM 1)					Total, % of SM
		WEL	WEF	AEL 2)	AEF	Loss 3)	
R$_o$ 35,000	Cellulose	1.1	27.1	0.6	26.5	7.3	35.5
	Other carbohydrates	5.9	1.7	0.2	1.5	11.1	18.7
	Non-carbohydrates	2.9	23.9	19.4	4.5	2.2	29.0
	Unknowns	4.5	8.5	1.7	6.8	3.8	16.8
	Total, % of SM	14.4	61.2	21.9	39.3	24.4	100.0
R$_o$ 35,000 (acetic acid extraction)		WEL	WEF	AcEL 4)	AcEF	Loss	
	Cellulose	1.1	27.1	-0.1	27.2	7.3	35.5
	Other carbohydrates	5.9	1.7	0.0	1.7	11.1	18.7
	Non-carbohydrates	2.9	23.9	15.4	8.5	2.2	29.0
	Unknowns	4.5	8.5	2.2	6.3	3.8	16.8
	Total, % of SM	14.4	61.2	17.5	43.7	24.4	100.0
R$_o$ 35,000 (ethanol extraction)		WEL	WEF	EtEL 5)	EtEF	Loss	
	Cellulose	1.1	27.1	0.5	26.6	7.3	35.5
	Other carbohydrates	5.9	1.7	0.4	1.3	11.1	18.7
	Non-carbohydrates	2.9	23.9	15.3	8.6	2.2	29.0
	Unknowns	4.5	8.5	2.1	6.4	3.8	16.8
	Total, % of SM	14.4	61.2	18.3	42.9	24.4	100.0

1) Total mass can be calculated either as WEL + WEF + Loss or as WEL + AEL + AEF + Loss
2) By difference from WEF - AEF
3) By difference from SM - (WEL + WEF)
4) By difference from WEF - AcEF
5) By difference from WEF - EtEF

5.1.5 *Clean Fractionation Concept*

5.1.5.1 Ideal Case

The clean fractionation concept must be based on a total mass and component-accounting procedure in relation to fractionation (table 21). In the ideal case (Figure 20), the mass retention of each of the three principal chemical components (cellulose, other carbohydrates, and non-carbohydrates) can be followed quantitatively through each of the three processing steps, steam explosion (Step 1), water extraction (Step 2), and delignification (Step 3). The solid fraction of each product, starting material (Stage 1), steam exploded fibers (Stage 2), water extracted fibers (Stage 3), and alkali extracted fibers (Stage 4) can be assessed using the same figure (Figure 20). If mass is lost (or gained) during a process step, it will be revealed by a line having a slope (during the particular processing step) which is related to the degree of mass removal. The line connecting the mass retention in the solid fraction at the beginning of the processing step with that at the end may have a slope that varies between 0 (complete mass retention) and “negative” 100 (complete mass loss, into solution state).

By steam explosion, all three chemical components pass through the steam explosion step without any mass loss, then, the three components enter into two process steps in which the three products are separated as two (completely) soluble fractions (WEL and AEL) and one insoluble fraction (AEF). Normalization of each slope, during each of the three process steps, to unity (or percent) produces a sequence of three numerical slopes that describe the cleanness of fractionation. For example, if the hemicelluloses (other carbohydrates) fraction has slopes of 0, 100, and 0 % for steps 1, 2, and 3, respectively, all hemicelluloses would have been released into the water extract in step 2. Any slope less than 100 % in step 2 would indicate loss of hemicelluloses during step 1 and/or retention of hemicelluloses in the stage 3-product, WEF. Thus, the absolute value of the slope parameter is a measure of process (i.e., fractionation step) cleanness, and this comes at the expense of another product impurity and cross-contamination.

Table 21. Mass retention of solid fiber fractions by stage (ideal case and red oak).

Treatment condition	Chemical component	Mass retention in solid fraction, % of SM			
		Stage 1, SM	Stage 2, SEF	Stage 3, WEF	Stage 4, AEF
Ideal Case	Cellulose	100.0	100.0	100.0	100.0
	Other carbohydrates	100.0	100.0	0.0	0.0
	Non-carbohydrates	100.0	100.0	100.0	0.0
R_o 5,000	Cellulose	100.0	87.5	85.3	76.3
	Other carbohydrates	100.0	72.7	26.2	11.2
	Non-carbohydrates	100.0	80.3	73.7	23.8
R_o 10,000	Cellulose	100.0	74.1	72.0	74.5
	Other carbohydrates	100.0	65.0	9.4	8.5
	Non-carbohydrates	100.0	77.7	68.1	14.8
R_o 15,000	Cellulose	100.0	72.0	69.5	70.0
	Other carbohydrates	100.0	59.9	8.2	5.8
	Non-carbohydrates	100.0	82.5	71.0	14.5
R_o 20,000	Cellulose	100.0	73.5	70.6	67.5
	Other carbohydrates	100.0	57.6	7.5	5.2
	Non-carbohydrates	100.0	82.4	68.6	17.3
R_o 35,000	Cellulose	100.0	79.6	76.6	74.8
	Other carbohydrates	100.0	41.0	9.1	8.1
	Non-carbohydrates	100.0	92.3	82.4	15.5
R_o 35,000 (acetic acid extraction)	Cellulose	100.0	79.6	76.6	74.8
	Other carbohydrates	100.0	41.0	9.1	8.1
	Non-carbohydrates	100.0	92.3	82.4	29.3
R_o 35,000 (ethanol extraction)	Cellulose	100.0	79.6	76.6	74.8
	Other carbohydrates	100.0	41.0	9.1	8.1
	Non-carbohydrates	100.0	92.3	82.4	29.5

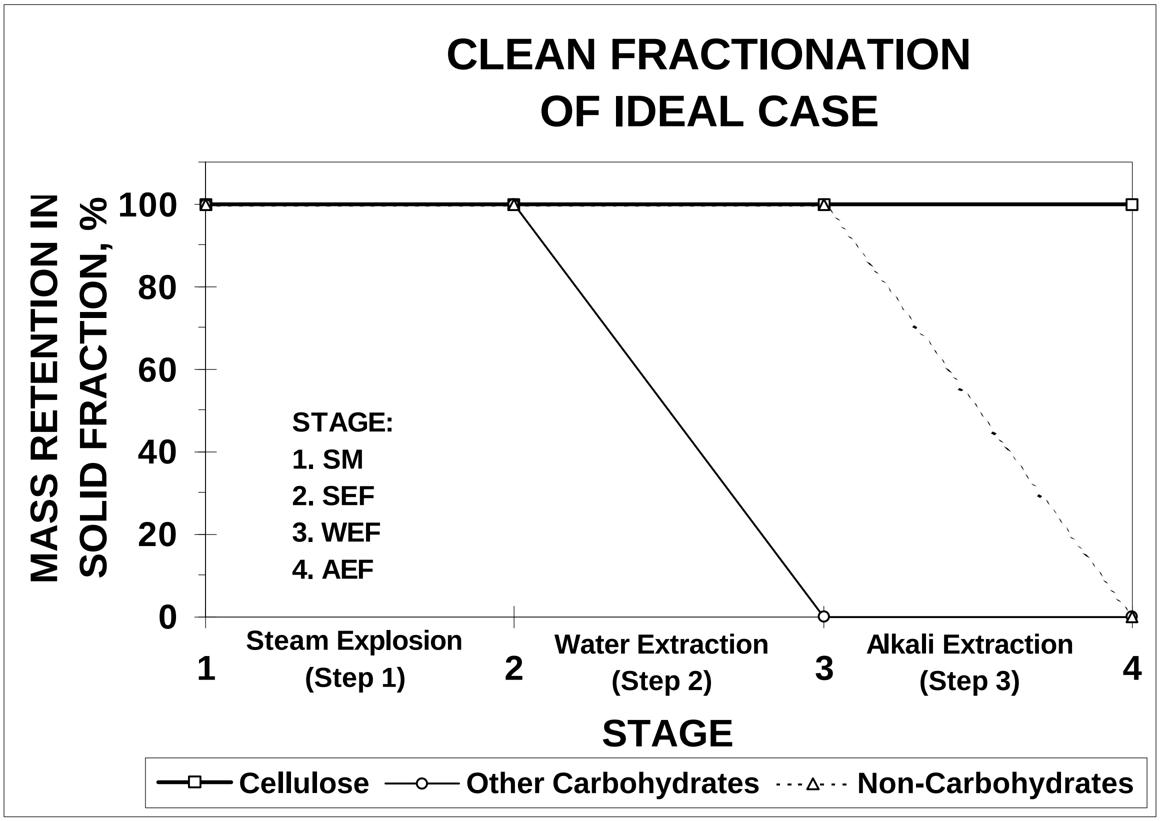

Figure 20. Plot of the clean fractionation scheme - ideal case scenario.

5.1.5.2 Series of Severity

The mass fractionation data and summative analysis results obtained with red oak chips during steam explosion experiments under severity conditions rising from R_o 5,000 to 35,000 are given in Tables 17 to 21. The fractionation behavior of the five steam exploded samples in relation to the clean fractionation concept is illustrated in Figures 21 to 27.

Each figure provides a quantitative assessment of the behavior of three principal wood components, cellulose, other carbohydrates and non-carbohydrates, during each of the fractionation process. The clean fractionation slope parameters for each component and during each process step at each severity factor are summarized in Table 22.

Cellulose losses in Step 1, steam explosion, reflect overall mass loss in this process step. This loss is greatest during moderate severity (R_0 15,000), and it is lower at either lower or higher severity. Cellulose remains virtually unaffected during water washing and alkali extracting.

The other carbohydrates component (hemicelluloses) of red oak is clearly susceptible to both steam explosion (Step 1) and water washing (Step 2). Whereas ideal behavior would require that other carbohydrates are released entirely into the water soluble fraction during steam explosion, this release reaches a maximum of 56 % at R_0 10,000 and it is lower at both higher and lower severities (Table 22). In a study with *Eucalyptus* wood, the maximum amount of soluble sugars occurred at Log R_o 3.9 (Ro 8,000).[34] In another study with *Populus tremuloides*, Zhuang and Vidal[46] reported that the highest yield of pentosans (70%) can be obtained at severities between Log R_o 3.8 to 4.0, Viggiano et al.[41] confirmed in their work with yellow that Log R_o 3.86 is an optimum severity to recover most pentosans (61 %).

Whereas the lower slope parameter (i.e., step 2) at lower severity (i.e., R_0 5,000) indicates significant hemicelluloses retention in the WEF-fraction leading to significant cross-contamination of the fraction solubilized during step 3 (alkali extraction), slope

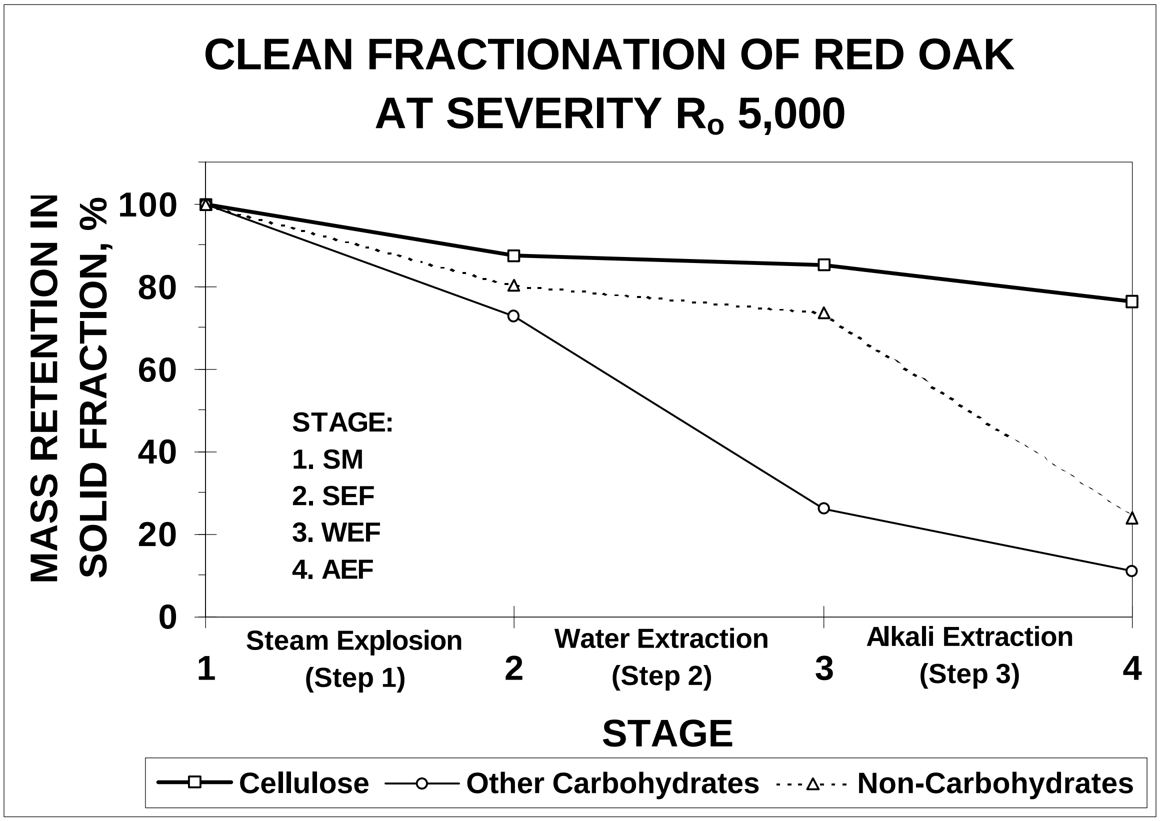

Figure 21. Plot of the clean fractionation scheme - red oak at R_o 5,000.

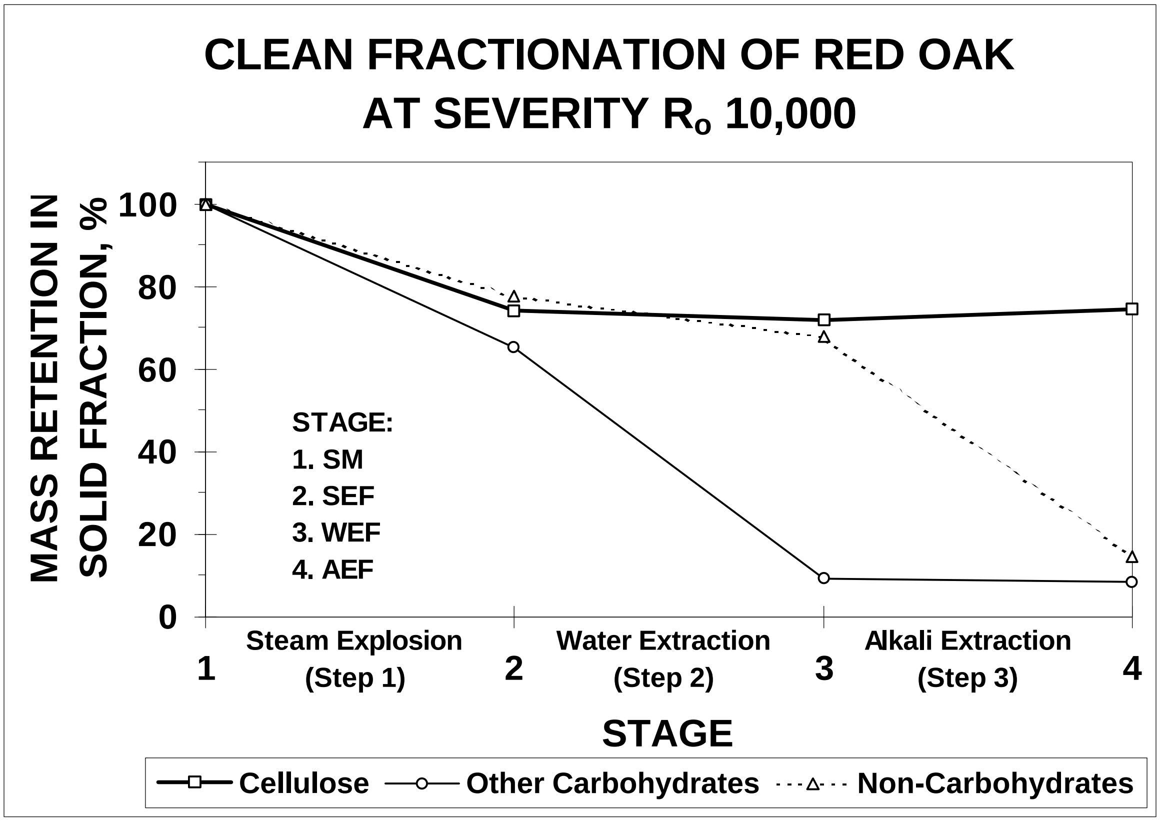

Figure 22. Plot of the clean fractionation scheme - red oak at R_o 10,000.

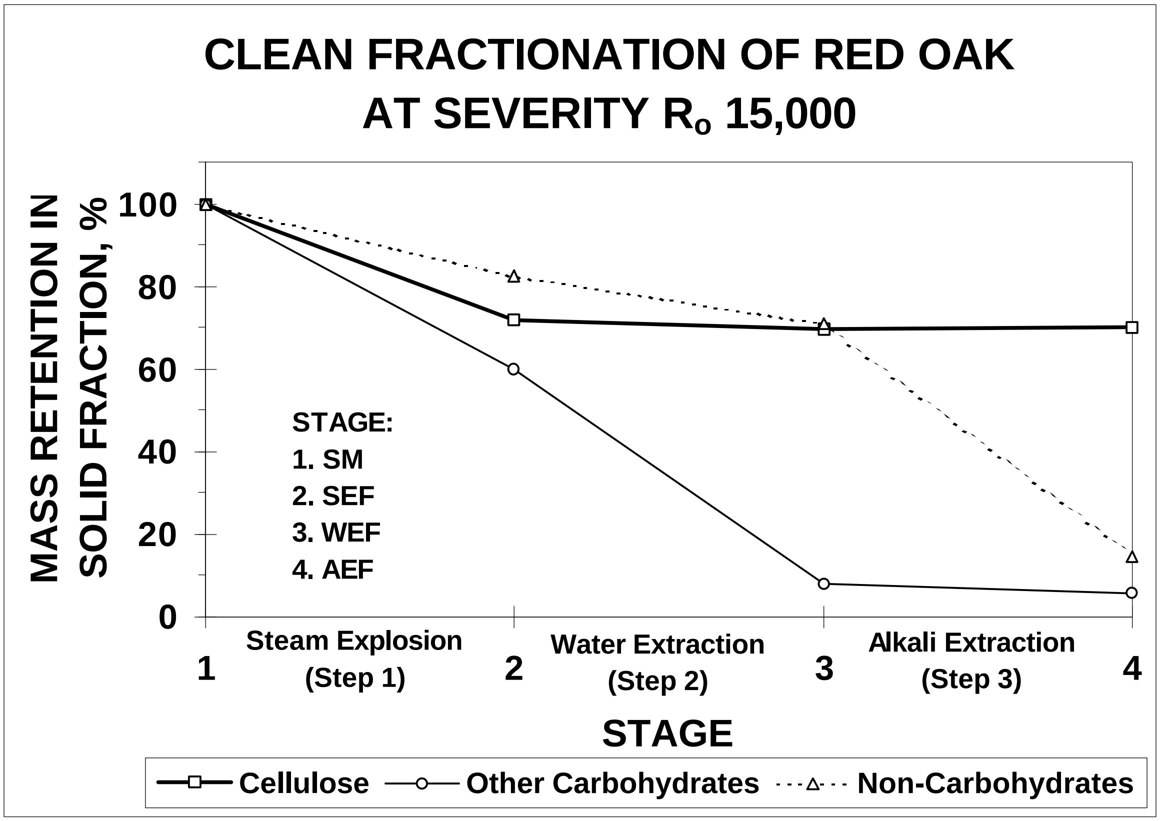

Figure 23. Plot of the clean fractionation scheme - red oak at R_o 15,000.

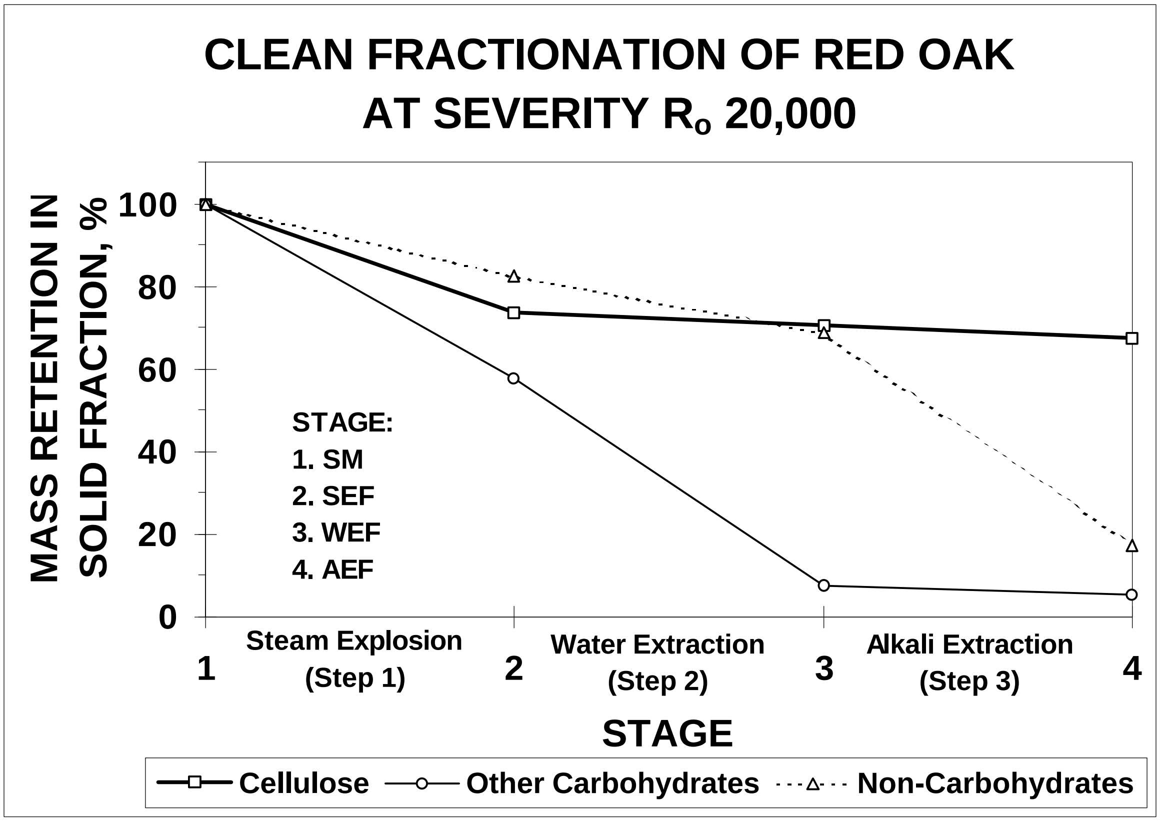

Figure 24. Plot of the clean fractionation scheme - red oak at R_o 20,000.

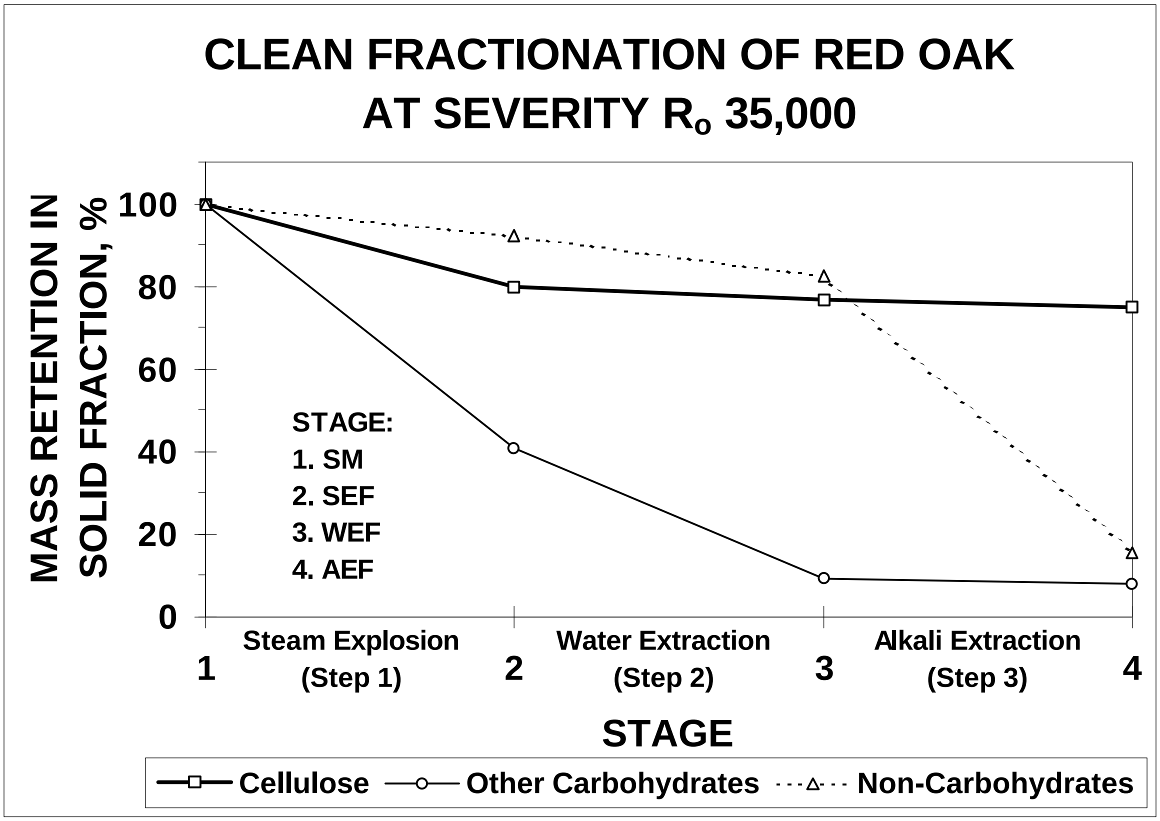

Figure 25. Plot of the clean fractionation scheme - red oak at R_o 35,000.

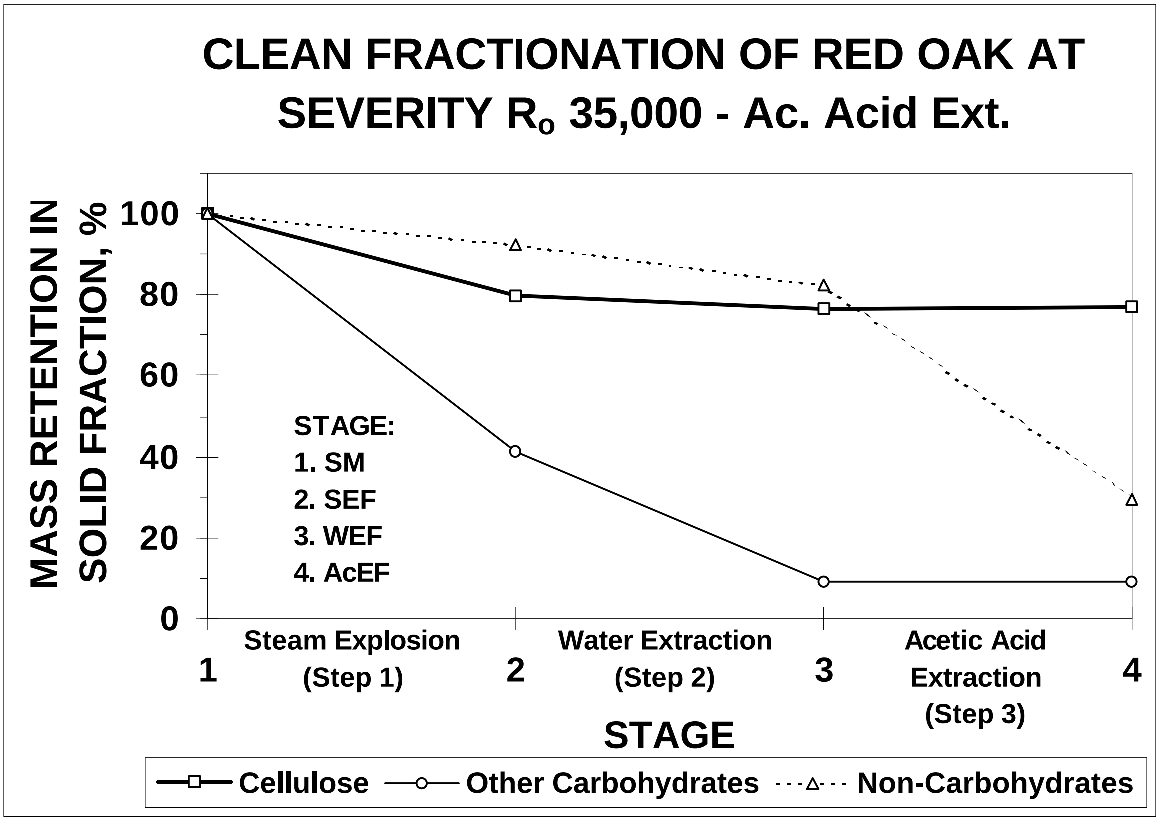

Figure 26. Plot of the clean fractionation scheme - red oak at R_o 35,000 (acetic acid).

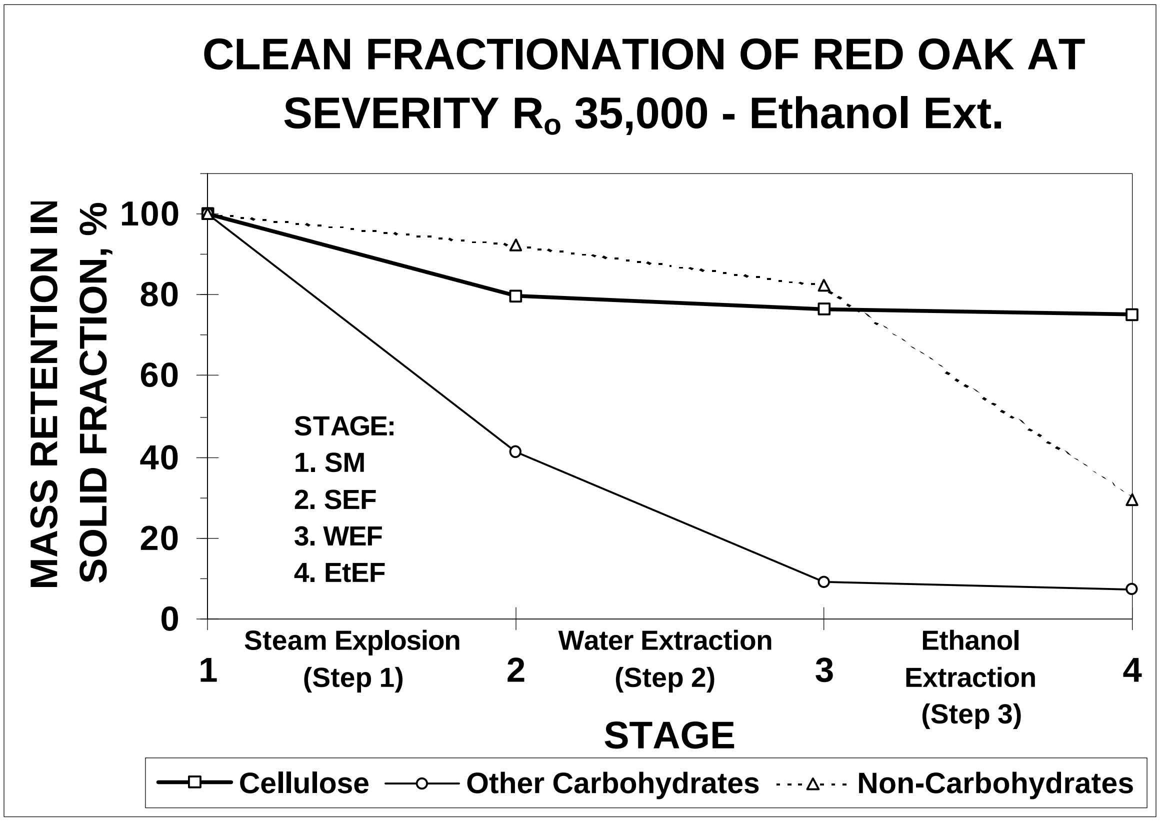

Figure 27. Plot of the clean fractionation scheme - red oak at R_o 35,000 (ethanol).

Table 22. Comparison of clean fractionation slope parameters of red oak1).

Severity / Step	Chemical component, % of mass lost per step			Total lost from Loss fraction data, % of SM
	Cellulose	Other carbohydrates	Non-carbohydrates	
R_o 5,000 / 1	12.6	27.4	19.7	16.9
R_o 5,000 / 2	2.1	46.4	6.6	
R_o 5,000 / 3	9.1	15.0	49.9	
R_o 10,000 / 1	25.8	35.0	22.3	22.6
R_o 10,000 / 2	2.5	55.6	9.7	
R_o 10,000 / 3	-2.8	1.0	53.3	
R_o 15,000 / 1	28.0	40.1	17.5	25.8
R_o 15,000 / 2	2.5	51.7	11.6	
R_o 15,000 / 3	-0.5	2.4	56.4	
R_o 20,000 / 1	26.5	42.4	17.6	24.6
R_o 20,000 / 2	2.9	50.1	13.9	
R_o 20,000 / 3	3.1	2.4	51.2	
R_o 35,000 / 1	20.4	59.0	7.7	24.4
R_o 35,000 / 2	3.0	31.9	9.9	
R_o 35,000 / 3	1.8	1.0	66.9	
R_o 35,000 / 3 2)	-0.1	-0.1	53.1	24.4
R_o 35,000 / 3 3)	1.6	2.1	52.8	24.4

1) Normalized to 100 % mass loss per step.

2) Acetic acid extraction.

3) Ethanol extraction.

reduction during step 2 processing at higher severities is clearly associated with the formation of increasingly larger amounts of degradation products during steam explosion. This must in all likelihood be attributed to increasing volatilization (as furaldehydes) during steam treatment as all but the lowest severity have a near 0 slope during step 3-processing.

The greatest slope parameter for non-carbohydrates expectedly occurs during step 3-processing (alkali extraction) where it increases with severity to a high of 67 %. The slope parameter of non-carbohydrates are 20 % during steam explosion at low severity and 5-15 % during step 2-processing at moderate to high severity (Table 22). Comparing delignification (step 3-processing) for the steam exploded mulch treated at highest severity (R_0 35,000) between alkali, aqueous ethanol, and aqueous acetic acid (Table 23), the data reveals that alkali is clearly superior to aqueous acetic acid and aqueous ethanol in terms of fractionation capacity, and that there is no significant difference between acetic acid and ethanol.

The consistent negative slopes during step 1-processing (steam explosion) have previously been attributed to mass loss during product collection. This mass loss averaged approximate 25% of total mass (Table 17). The fact that the slope parameters during step 1-processing vary, in part significantly, between the three principal components, with other carbohydrates having consistently larger slope parameters than cellulose and non-carbohydrates having lesser slopes, seems to suggest that some of the volatilized other carbohydrates (furaldehyde) condense with non-carbohydrates especially at high severity. This has the consequence of producing elevated lignin of SEF and WEF-products. This is consistent with experimental observations reported elsewhere by others.[18,35]

An evaluation of the negative slope parameters for the three principal red oak components on the scale of severity, R_0, allows the following conclusions (Figure 28). Cellulose maintains a virtually flat slope during all three processing steps at all severity levels (with the absolute slope value being related to the magnitude of overall mass losses); and the hemicelluloses component reaches a maximum of 56 % during step 2-processing at modest severity (R_0 10,000) and nearly 93% during step 1 and step 2-

processing combined. This means that the product of step 2-processing, WEF-solids, has extremely low contamination by other carbohydrates. Non-carbohydrates, by contrast, reach a maximum slope parameter of 67% during step 3-processing at the highest severity (R_0 35,000). Non-carbohydrates solubility in water (losses during step 2-processing) remain modest at all severities. Again, the fact that the slope parameter for the hemicelluloses component remains constant and very high for the combined process steps 1 and 2 while declining with severity during step 2-processing alone indicates that hemicelluloses are progressively lost to furaldehyde(s) formation and possible condensation with non-carbohydrates.

Table 23. Comparison of lignin extraction data (red oak, R_o 35,000).

Lignin extraction treatment	Step 3 - Slope parameter
20 % Alkali	66.9
80 % Acetic acid	53.1
70 % Ethanol	52.8

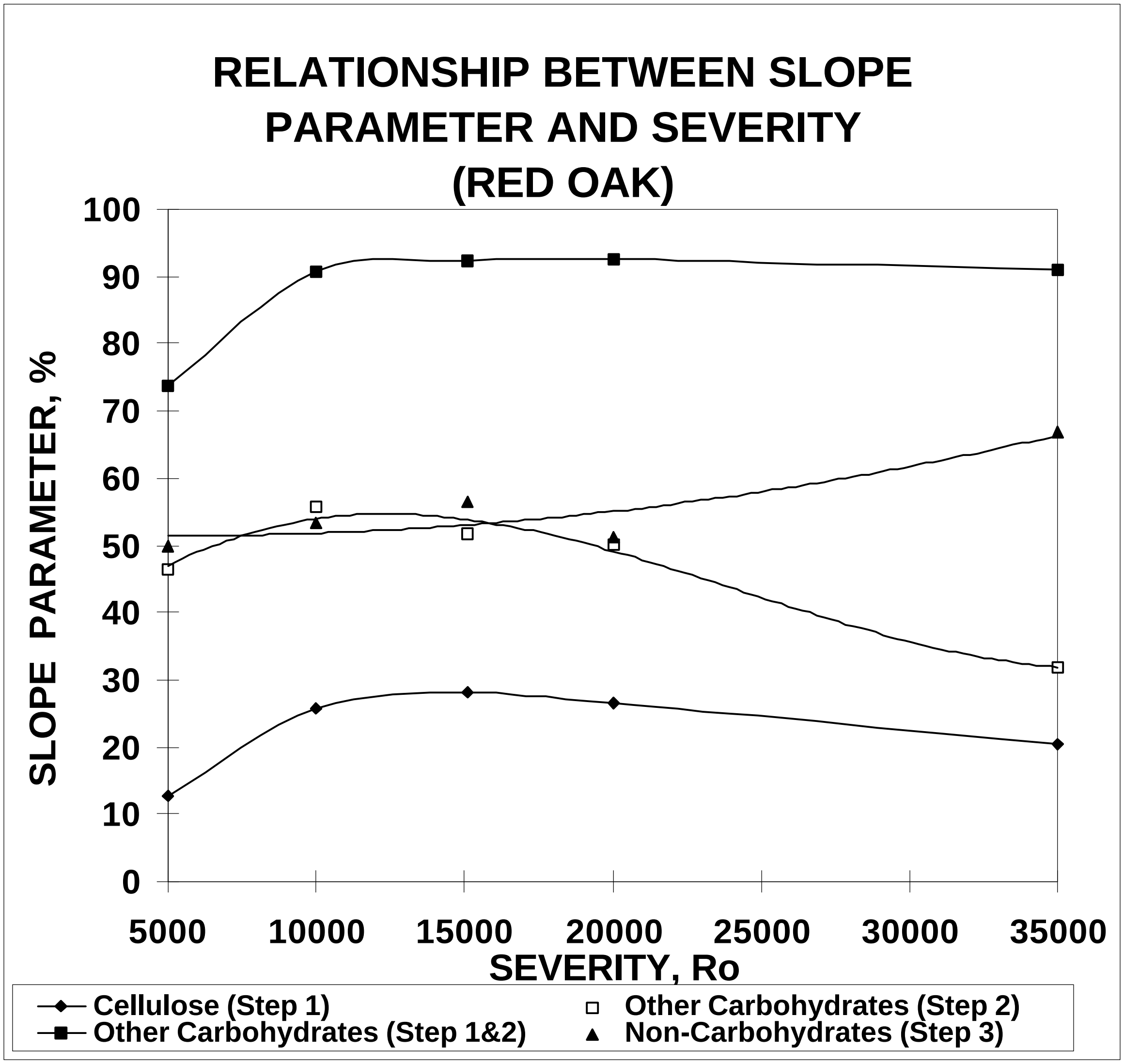

Figure 28. Relationship between maximum slope parameters and severity of red oak for cellulose, non-carbohydrates and hemicelluloses (i.e., other carbohydrates) isolation.

5.2 Clean Fractionation of Oil Palm Trunk Solids

5.2.1 *Oil Palm Trunk Solids*

In Malaysia, the oil palm industry generates a number of by products and residues. One of the main residues is oil palm trunk (OPT) solids. Oil palm trees are cut down for replanting purpose after 25-30 years.

5.2.2 *Mass Fraction Flow*

Oil palm (*Elaeis guineensis*) trunk solids chips were provided by Universiti Sains Malaysia in Malaysia. The chips were steam exploded, water extracted and alkali extracted in the Thomas M. Brooks Forest Products Center of Virginia Tech. Unlike red oak, fractionation data of oil palm trunks solids (Table 24) were provided from prior work, and these were adopted to the clean fractionation concept. Since no data were provided for Loss fraction, SEF of each severity was used as reference in order to apply the clean fractionation concept. Based on three severity data, the highest severity (R_o 10,000), gives the lowest yield of WEF and AEF fractions. However, it provides the highest yield of WEL.

5.2.3 *Summative Analysis*

Chemical analysis data of oil palm trunk solids also provided by previous workers. Acid soluble and acid insoluble lignin in WEF were found to be approximately 25 % and 3 %, respectively (Table 25). Unlike red oak, oil palm trunk solids did provide evidence for galactose and arabinose, which were detected in WEF, WEL and AEF. The total furaldehyde(s) components were < 1.5 %. Among the sugar components, glucose and xylose were the major components that dominated the distribution.

In oil palm trunk solids, it was reported that it contains some amount of starch.[40] However, starch determination was not performed. According to the solubility of starch in water, it was assumed that all glucose that become available in the WEL fraction was declared as glucose from starch. To fit this assumption in presenting the availability of the starch in the oil palm trunk, the starch component is placed in the chemical composition table (Table 26). Cellulose contents in the fractions range between 20-40 % except in AEF fraction at R_o 10,000 which reaches 60 %. In general, percentages of other carbohydrates and non-carbohydrates at R_o 10,000 always extremely lower or higher compared to the percentages of other carbohydrates and non-carbohydrates at low severities (R_o 600 and 2,000).

Table 24. Mass fractionation data of oil palm trunk solids.

Treatment condition	Mass fraction, % of SM					
	SEF	Loss [1)]	WEF	WEL [2)]	AEF	AEL[2)]
R_o 600	100.0	-	79.3	20.7	54.3	25.0
R_o 2,000	100.0	-	83.9	16.1	54.9	29.0
R_o 10,000	100.0	-	60.2	39.8	31.2	29.0

1) Loss data are not available, SEF (from calculation) is used as reference.

2) Calculated by difference.

Table 25. Analysis data of oil palm trunk solids fractions.

Biomass fraction	Chemical composition of, % of biomass fraction [1]								
	AIL [2]	ASL [3]	2-F [4]	HMF [5]	Glu [6]	Xyl [7]	Gal [8]	Ara [9]	Man [10]
WEF-0.6	22.2	3.9	0.8	0.3	34.9	16.4	3.0	10.6	0.0
WEF-2	19.4	4.3	0.8	0.3	33.4	15.4	2.5	8.1	0.0
WEF-10	32.3	2.7	0.3	0.3	44.3	6.7	2.4	0.0	0.0
WEL-0.6	3.6	5.2	4.0	2.4	34.9	0.0	3.0	9.7	0.0
WEL-2	3.6	5.6	0.3	1.9	30.9	0.0	2.0	3.9	0.0
WEL-10	4.3	7.7	1.2	1.1	14.1	16.0	2.1	7.3	0.0
AEF-0.6	15.5	3.7	0.7	0.3	41.4	17.3	2.2	8.4	0.0
AEF-2	18.8	3.5	0.8	0.3	41.1	16.8	2.7	7.9	0.0
AEF-10	16.2	1.6	0.2	0.4	66.2	0.0	0.0	7.3	0.0

1) Average of 2 replication data
2) Acid insoluble lignin/tannins
3) Acid soluble lignin/tannins
4) 2-furaldehyde
5) 5-(hydroxymethyl)-2-furaldehyde
6) Glucose
7) Xylose
8) Galactose
9) Arabinose
10) Mannose

Table 26. Chemical composition of oil palm trunk solids fractions.

Biomass fraction	Chemical composition, % of biomass fraction				
	Starch	Cellulose	Other carbohydrates	Non-carbohydrates	Unknowns [1]
WEF-0.6	-	31.8	27.6	26.1	14.5
WEF-2	-	30.5	24.0	23.7	21.8
WEF-10	-	40.3	8.5	35.0	16.2
WEL-0.6	34.9	-	11.7	8.8	44.6
WEL-2	30.6	-	5.6	9.2	54.6
WEL-10	14.3	-	24.0	12.0	49.7
AEF-0.6	-	37.7	25.6	19.2	17.5
AEF-2	-	37.4	25.3	22.3	15.0
AEF-10	-	60.2	6.7	17.8	15.3
AEL-0.6 [1]	-	19.1	31.9	41.1	7.9
AEL-2 [1]	-	17.4	21.7	26.3	34.6
AEL-10 [1]	-	18.9	10.4	53.5	17.2

1) Calculated by difference

5.2.4 *Fractionation Assessment*

Although the oil palm trunk solids data are missing the Loss fraction as well as the chemical composition of SM, one can handle the outcome assessment by using the SEF as reference (Table 27). By using the assumption that glucoses in WEL are glucoses for starch chains, it shows that 5-7 % of SEF is starch. While the non-carbohydrates content is between 21-26 %, cellulose is about 25 %. Hemicelluloses content at low severities (R_o 600 and R_o 2,000) have averages about 23 % but at highest severity, the hemicelluloses component drops to about 15 %. At high severity, hemicelluloses have probably been condensed to lignin and unknowns because both components are slightly increased.

5.2.5 *Clean Fractionation Concept*

Based on the outcomes assessment, mass retention of solid and clean fractionation slope parameter data are listed in Tables 28 and 29. As seen in Figures 29-31, all lines are not connected to the stage 1 (SM). So, SEF is taking the place as reference. Therefore no information can be provided on the steam explosion step.

As assumed previously, the starch component of oil palm trunk is soluble in water. It is contained entirely in the WEL. Therefore, no starch is observed in the WEF, AEL or AEF fraction. In other words, starch is assumed to be recoverable completely in the WEL fraction, and all other fractions are considered to be free of starch (Figure 32). In this case, cellulose losses during steam explosion can not be explained. However, about 3 % of cellulose is gained from lowest to highest severity. Perhaps, this is caused by human error like splashing during handling the extraction for the lowest severity. Theoretically, no cellulose component will be lost or gained by alkali extraction step.

Only at high severity (R_o 10,000), about 65 % of the hemicelluloses component can be recovered in the WEL fraction. At low severity, about 90 % of hemicelluloses fraction is retained by the WEF fraction. As a consequence of this behavior (case of low severity), AEL and AEF fractions are contaminated with high amounts of hemicelluloses. Non-carbohydrates also shows a efficient recovery in AEL (high reduction of non-carbohydrates in AEF) when the severity reaches R_o 10,000. This suggests that (within R_o 600-10,000 range), R_o 10,000 provides the best treatment conditions for getting the cleanest cellulose fibers (AEF) due to the highest slope parameter of hemicelluloses and non-carbohydrates fractionation. The worst treatment condition for achieving this goal involves a severity of R_o 2,000.

Table 27. Outcomes assessment of mass fractionation and summative analysis data of oil palm trunk solids.

Treatment condition	Chemical component	Mass fraction, % of SEF				Total, % of SEF
		WEL	AEL	AEF	Loss	
R_o 600	Starch	7.3	0.0	0.0	-	7.3
	Cellulose	0.0	4.8	20.5	-	25.3
	Other carbohydrates	2.4	8.0	13.9	-	24.3
	Non-carbohydrates	1.8	10.2	10.4	-	22.4
	Unknowns	9.2	2.0	9.5	-	20.7
	Total, % of SEF	20.7	25.0	54.3	-	100.0
R_o 2,000	Starch	4.9	0.0	0.0	-	4.9
	Cellulose	0.0	5.0	20.6	-	25.6
	Other carbohydrates	0.9	6.3	13.9	-	21.1
	Non-carbohydrates	1.5	7.7	12.2	-	21.4
	Unknowns	8.8	10.0	8.2	-	27.0
	Total, % of SEF	16.1	29.0	54.9	-	100.0
R_o 10,000	Starch	5.7	0.0	0.0	-	5.7
	Cellulose	0.0	5.5	18.8	-	24.3
	Other carbohydrates	9.6	3.0	2.1	-	14.7
	Non-carbohydrates	4.8	15.5	5.5	-	25.8
	Unknowns	19.7	5.0	4.8	-	29.5
	Total, % of SEF	39.8	29.0	31.2	-	100.0

Table 28. Mass retention of solid fiber fractions by stage (oil palm trunk solids).

Treatment condition	Chemical component	Mass retention in solid fraction, % of SM			
		Stage 1, SM 1)	Stage 2, SEF 1)	Stage 3, WEF	Stage 4, AEF
R_o 600	Starch 2)		100.0	0.0	0.0
	Cellulose	-	100.0	100.0	81.0
	Other carbohydrates	-	100.0	90.0	57.2
	Non-carbohydrates	-	100.0	91.9	46.3
R_o 2,000	Starch 2)		100.0	0.0	0.0
	Cellulose	-	100.0	100.0	80.3
	Other carbohydrates	-	100.0	95.7	65.8
	Non-carbohydrates	-	100.0	93.1	57.3
R_o 10,000	Starch 2)		100.0	0.0	0.0
	Cellulose	-	100.0	100.0	77.4
	Other carbohydrates	-	100.0	34.8	14.3
	Non-carbohydrates	-	100.0	81.5	21.5

1) No data available for SM, therefore; SEF is used as reference for mass retention.

2) Soluble glucan in WEL is assumed as starch.

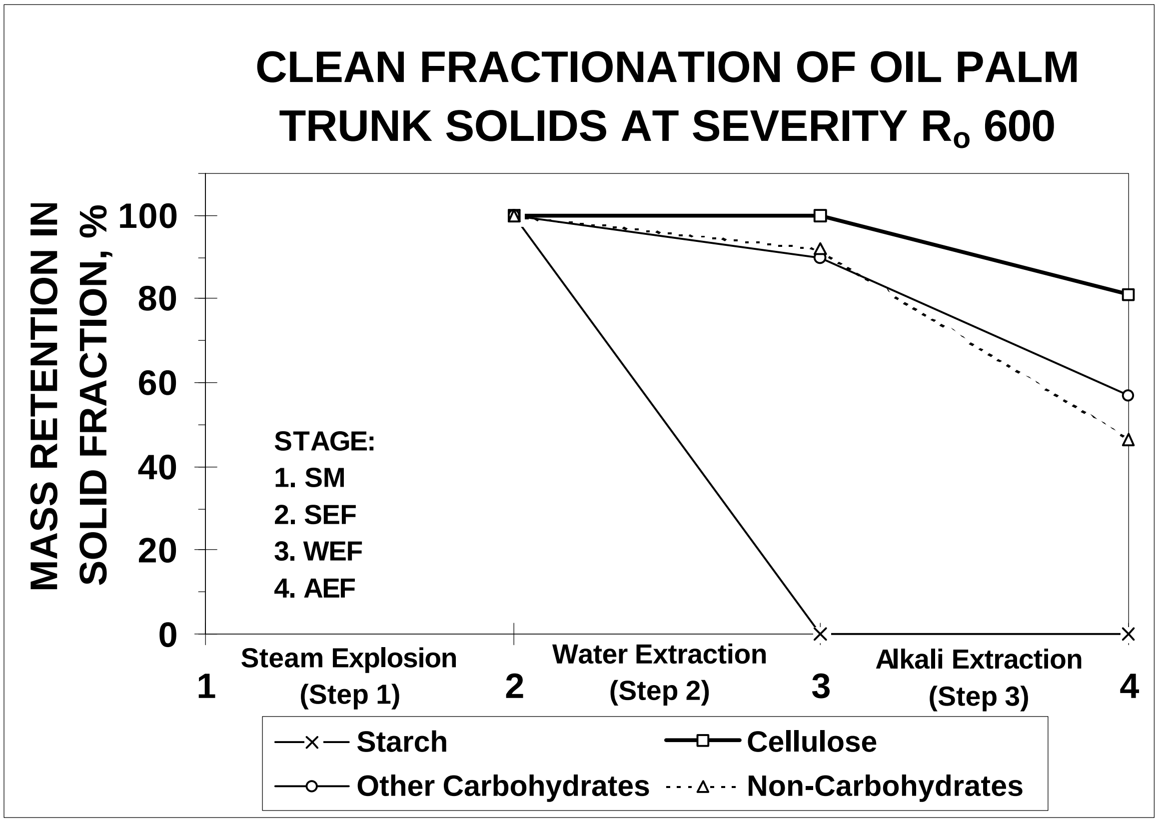

Figure 29. Plot of the clean fractionation scheme - oil palm trunk solids at R_o 600.

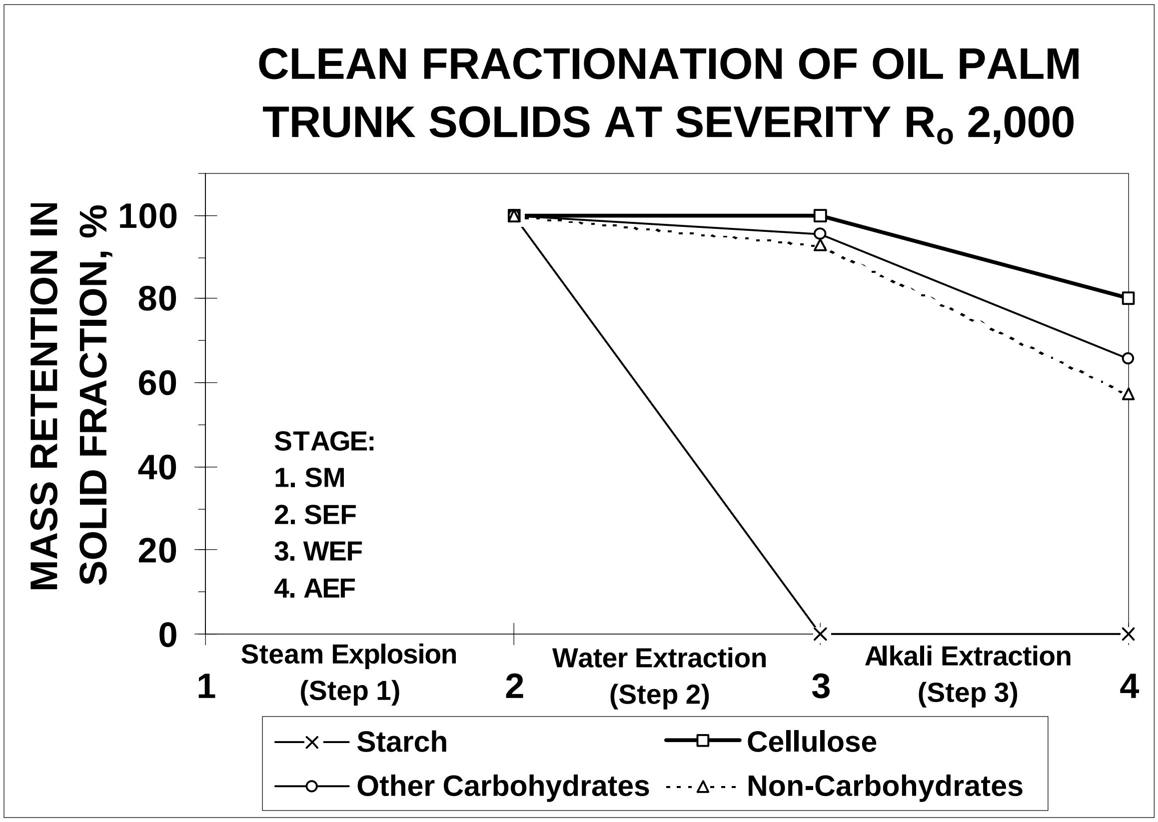

Figure 30. Plot of the clean fractionation scheme - oil palm trunk solids at R_o 2,000.

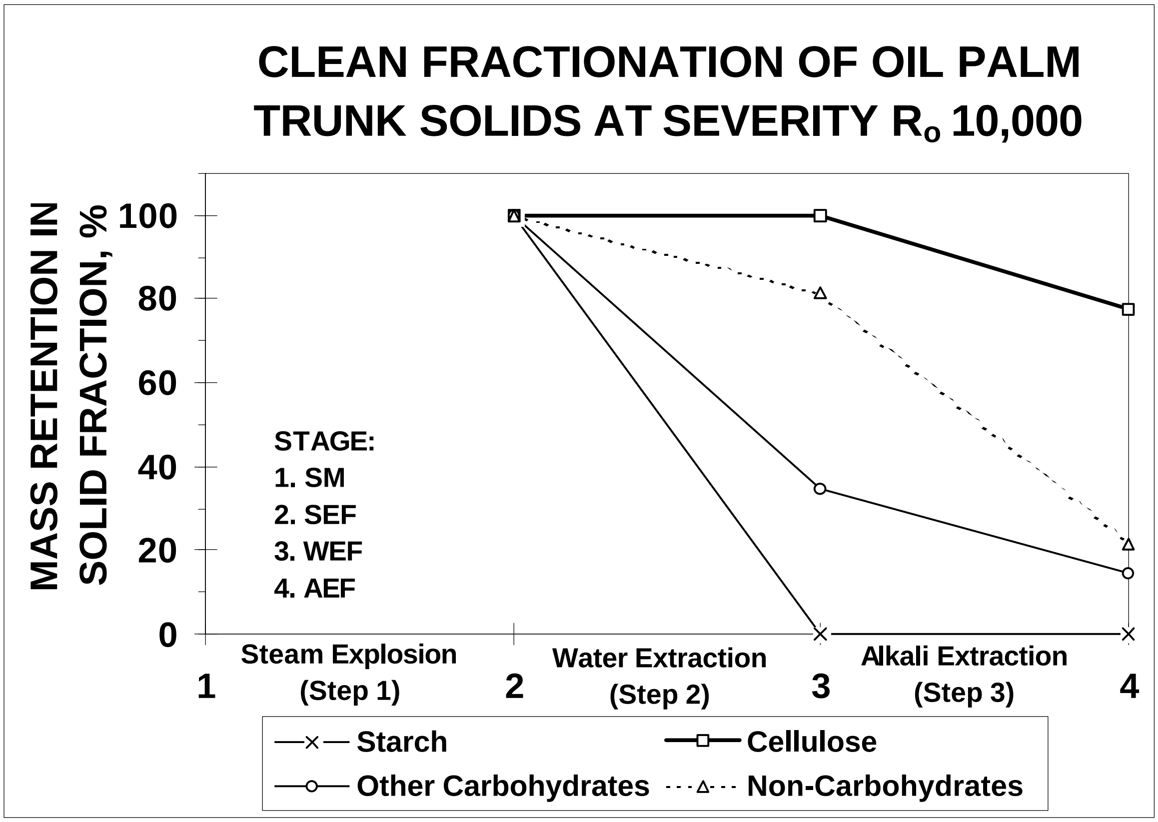

Figure 31. Plot of the clean fractionation scheme - oil palm trunk solids at R_o 10,000.

Table 29. Comparison of clean fractionation slope parameters of oil palm trunk solids 1).

Severity / Step	Chemical Component, % of mass lost per step			
	Starch	Cellulose	Other carbohydrates	Non-carbohydrates
R_o 600 / 1	-	-	-	-
R_o 600 / 2	100.0	0.0	10.0	8.1
R_o 600 / 3	0.0	19.0	32.9	45.6
R_o 2,000 / 1	-	-	-	-
R_o 2,000 / 2	100.0	0.0	4.3	7.0
R_o 2,000 / 3	0.0	19.7	29.8	35.8
R_o 10,000 / 1	-	-	-	-
R_o 10,000 / 2	100.0	0.0	65.2	18.5
R_o 10,000 / 3	0.0	22.6	20.5	60.0

1) Normalized to 100 % mass loss per step.

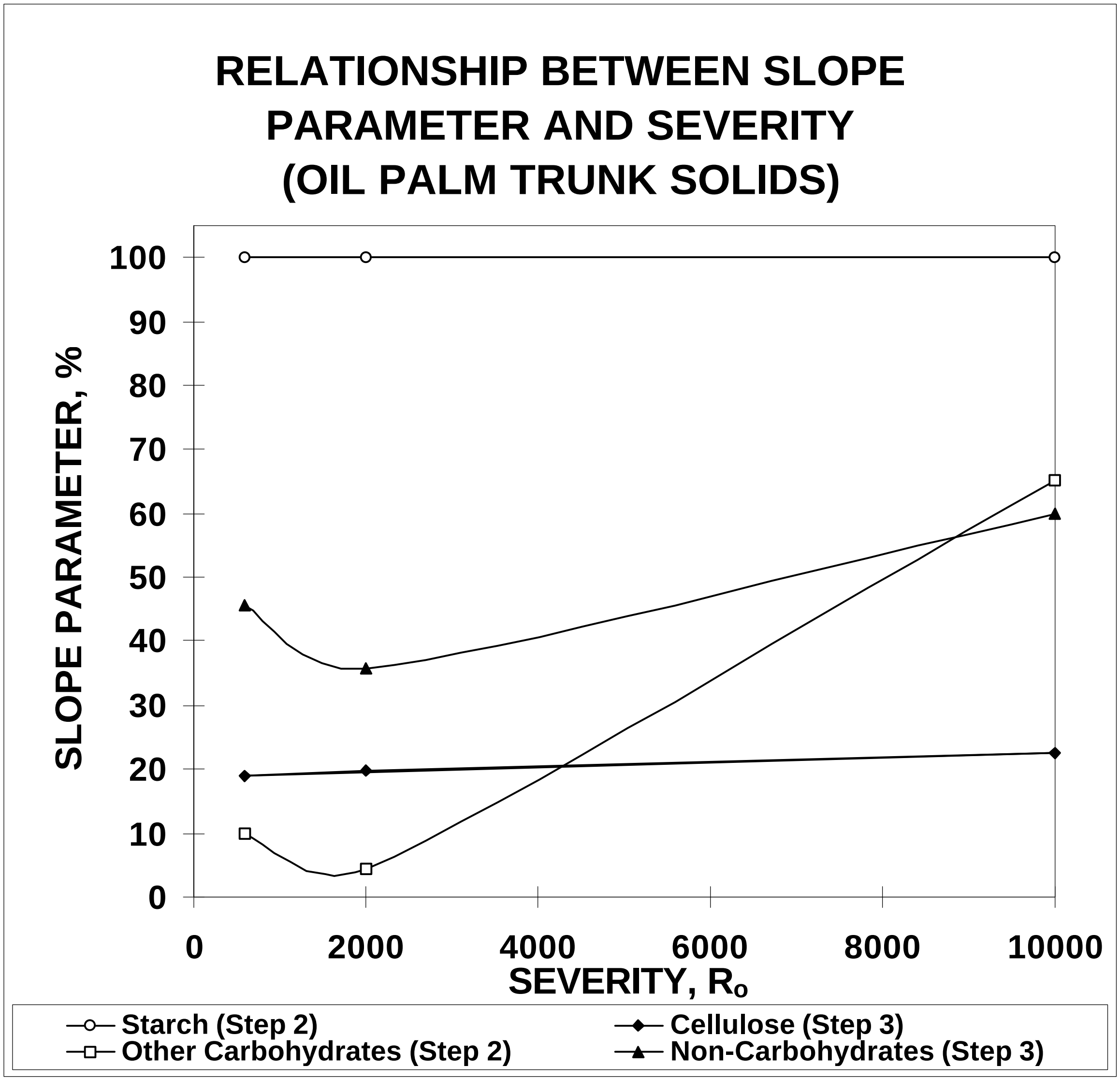

Figure 32. Relationship between maximum slope parameter and severity of oil palm trunk solids for cellulose, non-carbohydrates and hemicelluloses (i.e., other carbohydrates) isolation.

CHAPTER 6

6.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations of the study on clean fractionation of biomass materials are as follows:

i. Mass fraction distribution indicates that about 1/5 of total mass is not recoverable after steam explosion (red oak sample). To reduce the loss, running a larger sample is recommended. Any significant changes in the amount of losses will affect mass fraction and chemical composition data of the sample.

ii. Mass fractionation and summative analysis data always vary with raw material type, severity and perhaps amount of sample which was steam exploded.

iii. The clean fractionation diagram reveals that almost half of hemicelluloses (other carbohydrates) are lost during steam explosion (red oak sample). Only minor unrecoverable cellulose is lost (in the pipeline, cyclone and during collection). Within a series of severities above R_o 10,000, when the amount of hemicelluloses decreases in SEF, the amount of non-carbohydrates is increased. This suggests perhaps that volatile substances (degradation products of hemicelluloses) condense to lignin in the steam explosion step. There appears to be a relationship between an increase in the non-carbohydrates and a decrease in the other carbohydrates component.

iv. Based on the clean fractionation concept, water extraction is a quite reasonable method for the removal of other carbohydrates from SEF. In the case of red oak, only a small amount of other carbohydrates remains in WEF. However, a lot of other carbohydrates (40-50 %) are lost in the steam explosion process.

v. Among the delignification methods (alkali, acetic acid and ethanol extractions), on red oak sample, alkali extraction is the best method to eliminate non-carbohydrates from WEF.

vi. The clean fractionation concept is a useful tool to assist in understanding the effect of steam explosion and extractions on material composition. It opens a possibility to choose the right severity and extraction protocol to get a desired product. This concept also can be adopted to other fractionation techniques if mass fraction and chemical composition are determined.

vii. The chemical components in mass fraction distribution will be better defined if more analysis, like uronic acid and acetic acid determinations, are performed.

viii. The cleanest AEF of red oak can be produced (by removal of other carbohydrates and of non-carbohydrates) by steam explosion at a severity between R_o 10,000 and 15,000. While for the oil palm trunk solids, this is at R_o 10,000.