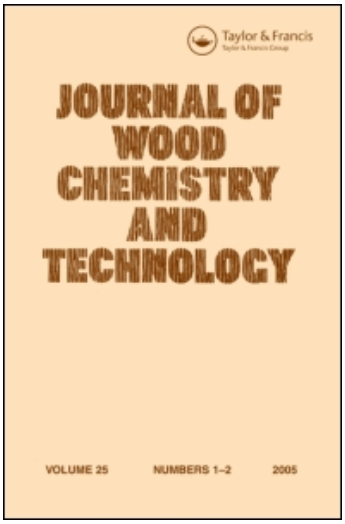

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Singh, Surendra and Roy, D. N.(1996) 'The Effect of Recycling on Chemical Properties of the Thermomechanical Pulp', Journal of Wood Chemistry and Technology, 16: 4, 421 — 437
To link to this Article: DOI: 10.1080/02773819608545824
URL: http://dx.doi.org/10.1080/02773819608545824

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(4), 421-437 (1996)

THE EFFECT OF RECYCLING ON CHEMICAL PROPERTIES OF THE THERMOMECHANICAL PULP

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ABSTRACT

This study was designed to elucidate the effect of recycling on the chemical properties of thermomechanical pulps made from mature and juvenile woods of black spruce, jack pine and eastern white cedar. The amounts of organics components and the concentrations of trace elements were examined on each recycle, up to four cycles. The extractive contents were decreased after each cycle with an overall reduction of 70 to 85%. In the case of lignin, the trend was different from cycle to cycle but was more or less the same for all pulps. The lignin was reduced by 5% after four cycles. The reverse trend was true with holocellulose. Calcium and manganese concentrations were reduced for all the pulps while chlorine and sodium had no specific trend. Aluminum concentration was too small to infer any trend. These variations were not dependent on species and age of the wood.

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INTRODUCTION

With the enhanced use of recycled fibres, it has become increasingly important to know how the fibre properties are affected by recycling. During the past 25 years, the effect of recycling on pulp properties has been investigated thoroughly. A literature review done by Howard[1], however, pointed out that it was rare to find two groups who used the same experimental method. Past studies have documented the effects of recycling on chemical pulp fibres but until recently, there has been little work done with mechanical pulps. Furthermore, except for the recent paper by Bouchard and Douek[2], no work has been reported on the change in the chemical properties on recycling with any type of pulp.

The main thrust of the research in the '60s and '70s was to understand the causes of the observed general trends. A considerable number of investigators examined what has been called the fundamental problem in recycling, i.e., how fibres are affected by recycling procedures, and what the resulting effects are in the paper made from these fibres. It has been shown that the principle cause of the change in the sheet properties is the reduced bonding ability of the fibres[3-6]. While the loss of intrinsic fibre strength has been observed by some researchers[7,8], it is, however, a lesser problem. On occasions it has been found not to change at all[9] and even to increase[10]. Reduced bonding ability, on the other hand, is a widely recognized phenomenon, and has traditionally been described as "irreversible hornification," implying a stiffening and/or hardening of the fibre. Not all pulps have the same recycling potential[5]. Scallan and Tigerström[4] have pointed out that high yield pulps (TMP, CTMP) can recover the ability to take up water following a drying treatment, while lower yield chemical pulp cannot. Boven et al.[11] also noted that mechanical pulp lost little of its physical properties in comparison to chemical pulp. It has also been theorised that the loss of bonding potential could be due to change in surface properties during recycling especially because of the removal of the hemicellulose from the surface of the fibre. It was speculated that during recycling, hydrogen bonding is inhibited, resulting in a loss in surface condition[12].

Inspite of such speculation about the possible effect of hemicellulose and lignin, there is very limited work reported on the chemical changes in the pulp fibres on recycling.

Yamagishi and Oye[13] have shown that the increase in the crystallinity index of recycled pulp ranges between 1.4 and 2.7% after four cycles. However, Bouchard and Douek[2] found no increase in cellulose crystallinity after recycling. During the beating of sulphite and sulphate pulps, 0.3-0.6% of the pulp carbohydrate, mainly xylan, were dissolved in the water as drying the pulps made xylan susceptible to dissolution[14]. Eastwood and Clarke[12] also reported of small solubilization of pentosans from a beaten semikraft pulp after recycling three times. It is generally believed that the dissolution of wood components results from both the mechanical action[15] and drying[14].

Heavy metals are known to decompose hydrogen peroxide, and thus to reduce peroxide bleaching efficiency[16]. Therefore, it would be worthwhile to know whether trace elements like iron, calcium, magnesium, aluminum, and chlorine, etc. bleed off or stay in the system during the recycling. Scallan and Grignon[17] observed that the presence of Na^{+} and Ca^{++} affects the surface properties and increases the ability of the fibres to bond extensively. Surprisingly, so far, no work, has been reported on the behavior of trace elements during recycling.

The relationship between the change in the chemical properties of recycled pulp and paper quality is not defined. This program was undertaken to provide background information on chemical changes during recycling.

EXPERIMENTAL METHODS

The raw materials used in this study were thermomechanical pulps (TMP) made from mature (>15 years) and juvenile (≤15 years) wood of black spruce (*Picea mariana*), jack pine (*Pinus banksiana*), and eastern white cedar (*Thuja occidentalis*). These pulps were made by Lee[18] at Abitibi Prices Research Centre,

Mississauga, Ontario. Pulps, stored at never-dried state at 4^0C, were hot disintegrated for latency removal (CPPA Standard Method C.8P[19]) before making the handsheets of 200 g/m^2 for recycling. The recycling process included sheet making, pressing, drying and disintegration. Sheets were made over filter paper (Reeve-Angel, #1, grade 230, 25 cm diameter) to retain all the fibres and fines. The Noble and Wood sheet making machine was used for pressing and drying. The wet webs were passed between two steel rolls at a constant pressure of 344.7kPa. Sheets were put in between two felts while passing through the steel rolls to avoid sheet crushing. After pressing, the sheets were dried over a rotating cylindrical dryer at surface temperature of 97-105^{0}C. Final moisture content in sheet was around 7-9%. For further recycling sheets were soaked overnight in deionized water and disintegrated by British sheet disintegrator for about 10 minutes. All the pulps were recycled four times without adding any chemical during recycling. All other variables associated with recycling were kept constant.

The extractives contents of the pulps were determined as per Tappi standard T204 os-76[20] with dichloromethane instead of usual alcohol-benzene because dichloromethane is more environmentally friendly. For holocellulose determination, the chlorite-acetic acid method used by Zobel *et al.*[21] was followed. In this method, the carbohydrate fraction (holocellulose) is isolated by removing lignin from extractive free samples. For determination of alpha-cellulose content in the pulp, 17.5% NaOH was used to dissolve the hemicelluloses. Klason lignin was determined according to the Tappi standard T 222 om-83[20]. In this method, the carbohydrates are hydrolysed and solubilized by 72% sulfuric acid. The acid-soluble lignin was measured on filtrate specimen collected from the Klason lignin test, following Tappi um-250[20]. The sum of acid-soluble and acid-insoluble lignins represents the total lignin content in the pulp samples. Elemental analysis was also performed on unextracted recycled pulp samples to assess the concentrations of Al, Ca, Cl, Cu, I, K, Mg, Mn, Na, Ti, V, and Zn by employing Instrumental Neutron Activation Analysis (INAA). This was carried out at the slowpoke reactor Facilities at the University of Toronto and involved a 10 kW, 5 minutes radiation

treatment with a 2 minutes delay time prior to 5 minutes of counting. All the results were corrected for moisture content in the sample.

RESULTS AND DISCUSSION

The percent contents of organic and inorganic constituents based on the total amount of the pulp of that cycle are presented in Table 1 and 2. Values obtained for each constituent were plotted versus the number of cycles, with the zero cycle corresponding to the virgin pulp. Trends of some major constituents were also plotted after normalizing the data to the fraction of the corresponding virgin pulp constituent.

Extractives

Extractives contents in all the virgin pulps were found to be lower (0.5 to 2.9%) as shown in Table 1, than reported in the corresponding wood (4 to 6%), perhaps mainly because of the removal of substantial amount of extractives during TMP manufacturing and latency removal. Extractives contents were gradually reduced from cycle to cycle of all the pulps as depicted in Figure 1 with an overall removal of 70 to 85 %, resulting in a very low residual extractives content. In Figure 2, a least square line is plotted for all the pulps together with normalized data by taking the mean of all the normalized values at each cycle. The statistical evaluations of these mean experimental data gave

$$y = 0.940 - 0.196\,x \qquad (>99\%,\ R^2 = 0.97)$$

where

y = estimated extractives (fraction of virgin pulp extractives) content

x = recycle number

It could be speculated, based on above regression equation, that most of the extractives will be removed after five cycles.

TABLE 1

Organic Chemical Constituents of Thermomechanical Pulp on Recycling

	Cycle #	Black Spruce[1]	Black Spruce[2]	Jack Pine[1]	Jack Pine[2]	E. W. Cedar[1]	E. W. Cedar[2]
Extractive	0	0.89	0.49	1.78	2.89	1.30	1.43
	1	0.79	0.40	1.05	1.96	0.84	0.86
	2	0.46	0.32	0.72	1.53	0.55	0.55
	3	0.38	0.24	0.57	0.86	0.44	0.35
	4	0.19	0.14	0.33	0.60	0.19	0.22
Holocellulose	0	73.6	73.9	72.9	72.5	71.8	72.7
	1	76.5	77.0	75.1	74.5	73.1	73.8
	2	74.9	77.1	75.7	73.8	74.5	74.4
	3	74.4	74.6	75.0	73.5	74.4	74.6
	4	76.5	77.1	76.3	75.0	75.4	76.0
Lignin	0	29.8	30.7	30.4	31.9	34.0	34.3
	1	28.5	28.7	29.8	30.8	32.9	33.3
	2	28.0	29.3	30.9	31.3	32.7	33.9
	3	29.3	29.6	29.4	30.5	32.3	31.7
	4	29.2	29.2	29.6	30.3	32.2	31.4

[1]mature [2]juvenile

Lignin

Lignin contents in all the virgin pulps were found to be slightly higher than reported in literature for the corresponding wood. However, results were in close agreement with that of Bouchard and Douek[2] and Chang et al.[22]. A higher relative percentage of lignin in virgin pulps is understandable because of the removal of considerable amounts of extractives during TMP manufacturing. The percent amounts of lignin in pulps after the first cycle was reduced by 0.5 to 2.0 % based

TABLE 2

Inorganic Trace Elements in Thermomechanical Pulp on Recycling

Pulp	Cycle #	Calcium (ppm)	Manganese (ppm)	Sodium (ppm)	Chlorine (ppm)	Aluminum (ppm)
Black Spruce (mature)	0	1054	78	45	72	2
	1	983	70	78	94	4
	2	939	69	66	80	3
	3	922	54	85	86	3
	4	946	65	82	76	3
Black Spruce (juvenile)	0	861	111	57	84	2
	1	840	71	85	92	3
	2	781	66	88	75	4
	3	790	62	96	78	4
	4	730	59	80	65	4
Jack Pine (mature)	0	694	68	41	61	2
	1	641	34	56	69	3
	2	587	32	46	63	3
	3	551	30	45	56	3
	4	531	29	58	60	3
Jack Pine (juvenile)	0	681	53	44	53	3
	1	601	31	55	80	4
	2	606	30	48	75	4
	3	590	28	50	65	5
	4	561	26	44	60	5
E.W.Cedar (mature)	0	1130	4	30	46	1
	1	1000	3	50	68	4
	2	957	2	46	61	5
	3	869	2	56	66	5
	4	902	2	41	59	5
E.W.Cedar (juvenile)	0	1300	5	47	77	1
	1	907	3	40	47	3
	2	860	3	48	50	3
	3	830	3	71	65	4
	4	804	3	54	53	4

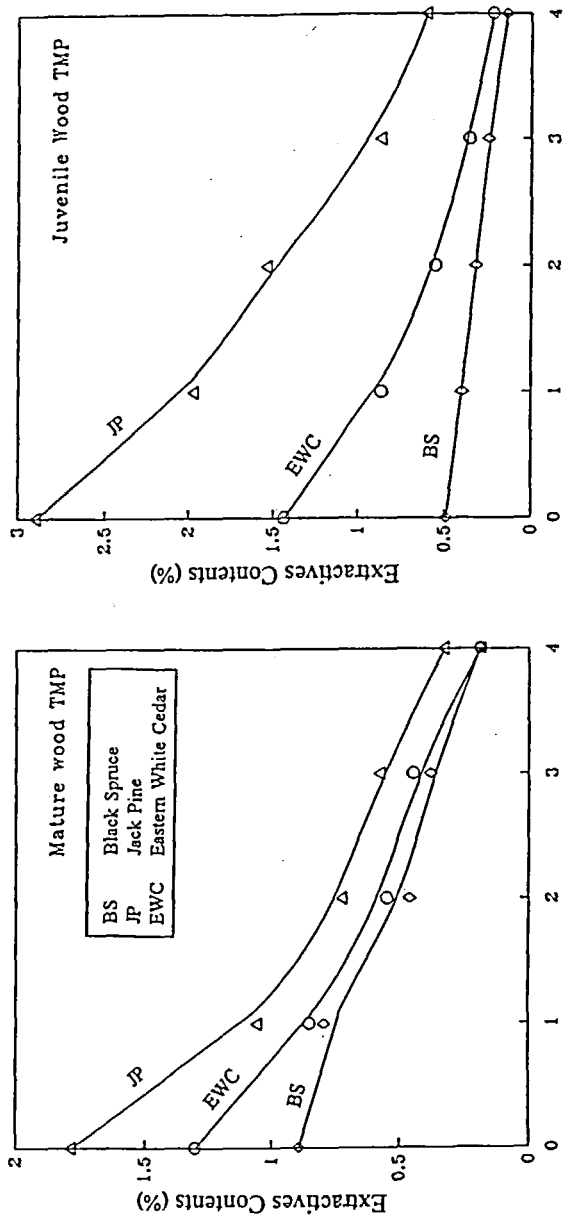

Figure 1. Effect of recycling on extractives contents

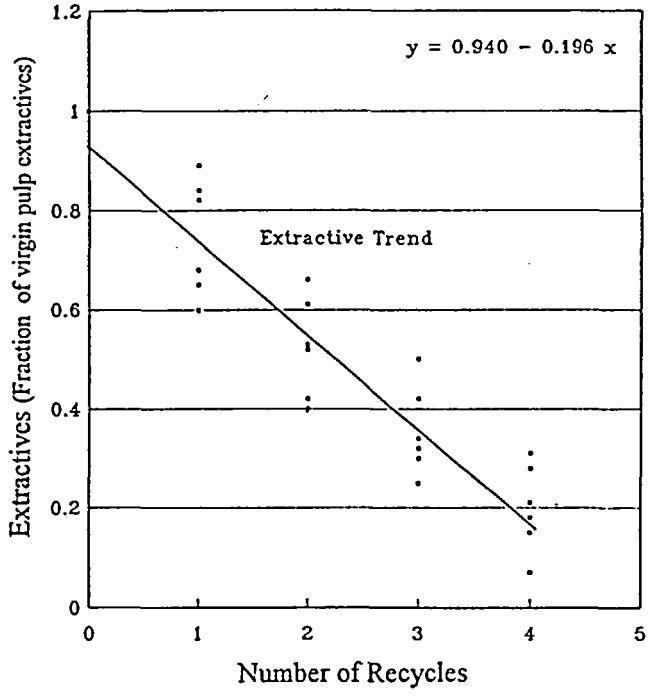

Figure 2. Trend of extractives contents upon recycling

on pulp. This reduction was true with all the pulps (Figure 3). A least square line, plotted in Figure 4, gave

$$y = 0.991 - 0.011\,x \qquad (>92\%, R^2 = 0.73)$$

where

y = estimated lignin (fraction of virgin pulp lignin) content

x = recycle number

The above equation indicates the reducing trend of lignin content on recycling. After four cycles the lignin content was around 0.95 (0.991 - 0.011 x 4) of the virgin pulp lignin content. In other words, 5% lignin based on lignin had left the pulp after four cycles which agrees with the finding of Bouchard and Douek[2] who reported a 6% reduction of lignin content after five cycles in TMP of eastern spruce.

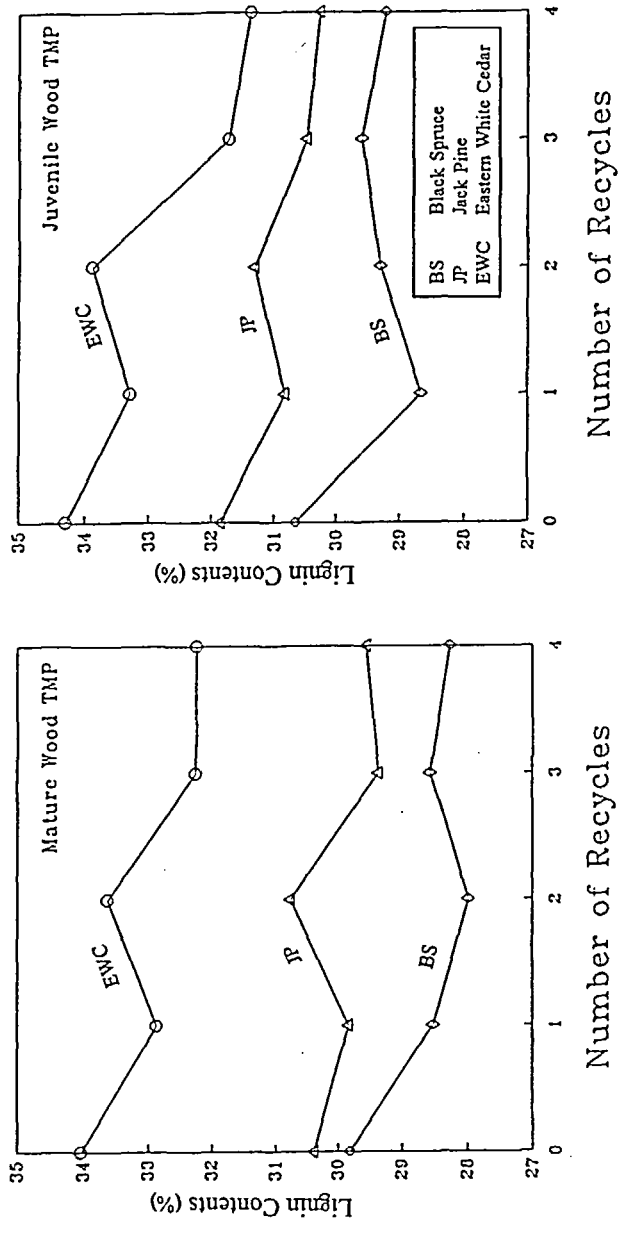

Figure 3. Effect of recycling on lignin contents

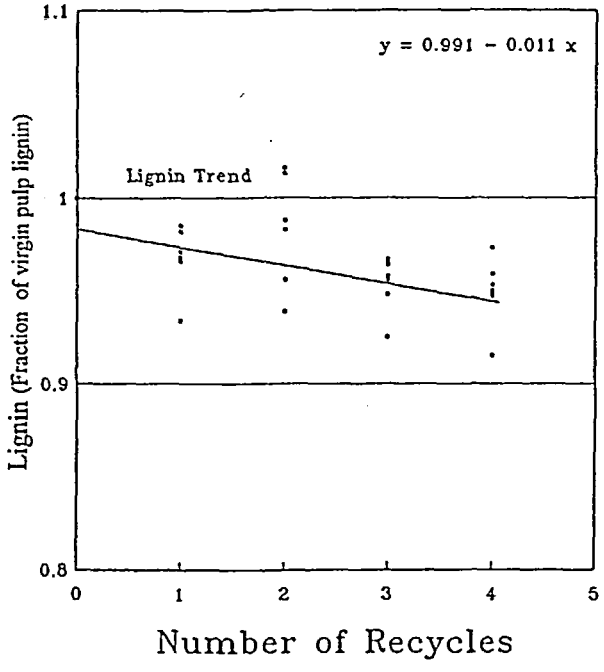

Figure 4. Trend of lignin contents upon recycling

The removal of the lignin during recycling can be explained on the basis of the mechanism of TMP manufacturing and the properties of mechanical pulp fines. In mechanical defibring, the fines are produced at the point where fibres turn loose, mainly from lignin-containing bordering layers, because refining at higher temperature tends to split the trachields along the region between the middle lamella and the primary cell wall, resulting in mostly "intact" fibres coated with lignin[22]. On continuing refining, lignin will peel off from the surface of the fibre. The short portion of the pulp will contain the short and peeled fibres, fibrillated fibres and ray cell segment, as well as free floating particles[22]. As most of the fines originate from the lignin-containing middle lamella and the primary wall, one would expect to observe a relatively high concentration of lignin in the fines. This

trend would be enhanced by the high lignin content of ray cells, which are concentrated in the fines[23]. Thus gradual removal of fines, as TMPs are very sensitive to the loss of fines[24], during recycling could be one reason why the lignin content of the pulp diminishes on recycling.

A second reason could be solution of the lignin. In TMP, the wood is subjected to considerable chemical stresses. It is likely that after such severe treatment, a fraction of the lignin will be degraded. Some of this degraded lignin will be dissolved cycle to cycle. The rapid loss of lignin after the first cycle is probable due to the loss of lignin rich fines. The subsequent irregularity in the overall downward trend may arise from variations in the ratio of lignin to hemicellulose dissolution during recycling.

Holocellulose

Holocellulose content increased with recycling, contrary to the results of Bouchard and Douek[2] who reported a 5.3% loss of pentosans from eastern spruce TMP. By plotting the data for holocellulose as for lignin (Figure 4), we obtained Figure 5, which gave the least square line

$$y = 1.009 + 0.008\,x \qquad (>90\%,\ R^2 = 0.70)$$

where

y = estimated holocellulose (fraction of virgin pulp holocellulose) content

x = recycle number

The above equation gives an increase of 4% in the holocellulose content after four cycles. Interestingly, a similar trend ($y = 1.010 + 0.012\,x$, >92%, $R^2 = 0.71$) was found for the alphacellulose content. It is clear that the 4% increase in holocellulose content is simply a mirror image of the 5% decrease in lignin content. It seems therefore that, during recycling, both lignin and holocellulose are lost by fines removal and by solution; but, proportionately, more lignin is lost than holocellulose which results in the observed trends in the chemical constituents of the recycled fibre.

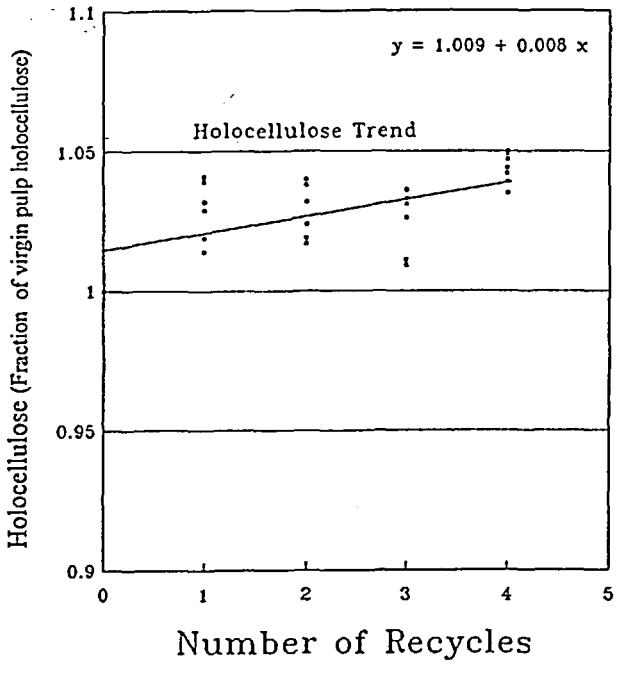

Figure 5. Trend of holocellulose contents upon recycling

Trace Elements

Metallic elements are often absorbed from the soil into the tree through the root system and are transported to all the areas within the growing tree. The variations in the trace element concentrations were also studied as they can affect the surface properties of the fibres and also the white water chemistry and it's utilization. Concentrations of Ca, Mn, Na, Cl and Al were measured for all the pulps on repetitive recycling. However, the presence of Ti, Fe, Zn, Mg, Cu, V, and K could not be detected by neutron activation analysis since the concentrations were below the minimum detection limit. Calcium and manganese concentration were reduced for all the pulp on recycling. This could be explained by the removal of fines of middle lamella and ray cell as these areas are rich in calcium and

TABLE 3

Statistical Summary of the Effect of Recycling on Chemical Constituents of Thermomechanical Pulp

Dependent Variables	R^2	F-Value	Pr > F
Extractives	0.92	91.45	0.0001**
Lignin	0.55	9.43	0.0001**
Holocellulose	0.70	16.42	0.0001**
Trace Elements			
Calcium	0.47	5.63	0.0023**
Manganese	0.64	11.48	0.0001**
Aluminum	0.44	4.93	0.0045**
Sodium	0.27	2.36	0.0803
Chlorine	0.10	0.67	0.6182

** Significant at 99% confidence interval

manganese concentration[25]. Moreover, removal of calcium could be linked to the removal of lignin as their distributions are parallel to each other[25,26]. Concentrations of sodium and chlorine were increased after first cycle in all the pulp, probably because of external contamination. However, after first cycle there was no clear trend. Aluminum concentration was too small to infer any trend.

Effect of Species and Wood Age

It is evident from Table 3 that recycling has a definite effect on the major chemical constituents of the pulp. However, no statistical significant differences were noted for different species (Table 4) or wood type (Table 5). This indicates that the effect of recycling on chemical properties was not dependent on species and age of the wood.

TABLE 4

Statistical Summary of the Effect of Species on Chemical Constituents of Thermomechanical Pulp during Recycling

Dependent Variables	R^2	F-Value	Pr > F
Extractives	0.04	0.46	0.7136
Lignin	0.13	1.54	0.2227
Holocellulose	0.07	0.75	0.5319
Trace Elements			
Calcium	0.25	4.52	0.0199
Manganese	0.15	2.32	0.6973
Aluminum	0.46	11.61	0.0002**
Sodium	0.23	4.05	0.0289
Chlorine	0.04	0.52	0.5985

** Significant at 99% confidence interval

TABLE 5

Statistical Summary of the Effect of Wood Age on the Chemical Constituents of Thermomechanical Pulp during Recycling

Dependent Variables	R^2	F-Value	Pr > F
Extractives	0.00	0.00	0.9883
Lignin	0.05	1.78	0.1914
Holocellulose	0.05	1.67	0.2052
Trace Elements			
Calcium	0.02	0.60	0.4449
Manganese	0.01	0.35	0.5566
Aluminum	0.02	0.68	0.4149
Sodium	0.08	2.40	0.1327
Chlorine	0.12	3.97	0.0562

CONCLUSION

Recycling had an effect on all the major chemical constituents of thermomechanical pulps, regardless of species and age of the wood. Extractives and lignin contents decreased while holocellulose content increased. It is important to note that an increase in overall holocellulose content does not mean that there was no loss of it. The extractives and lignin were likely removed to a higher extent than the holocellulose. Among the trace elements, only Ca and Mn showed significant changes. The data obtained here would represent the quantitative effects of recycling and thus provide a basis for future work aimed at analyzing the dissolved matters after each cycle.

ACKNOWLEDGMENTS

Sincere appreciation is extended to Dr. D. A. I. Goring for his invaluable suggestions and constructive help at various stages of the work. Authors also wish to express their appreciations to Abitibi Price Inc. for enabling the use of their research facilities.

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