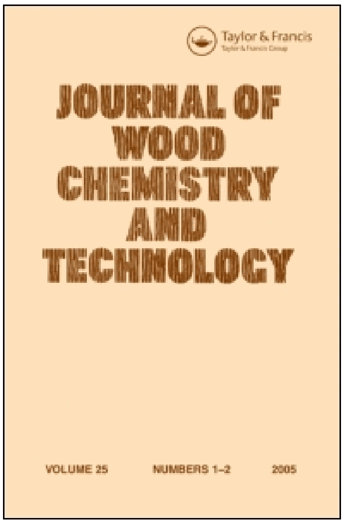

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SUITABILITY OF HYBRID WILLOW AS A SOURCE OF PULP

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ABSTRACT

Hybrid willow (Salix spp.) is a potential source of pulp as demonstrated by its fibre morphology, chemical composition and pulping kinetics. Fibre length and cell wall thickness measurements on one and two years old clones ranged from 0.49 mm to 0.70 mm and 2.5 μm to 3.6 μm respectively. Fibre length variation by annual growth layer varied from 0.5 mm in the first growth layer to about 1.1 mm in the last growth layer and the maximum growth rate occurred in the first two to three years for fourteen years old clones. The clones were producing more fibre fraction as indicated by volumetric composition. The UV absorptivities of milled wood lignin was found in the range of 12.17 - 14.31 $L.g^{-1}cm^{-1}$ at 278 nm and the presence of syringyl and guaiacyl lignin was observed. ^{13}C-NMR results of acetylated milled wood lignin showed clonal structural variations during lignification process and the Klason lignin content of one and two years old clones ranged from 20.8% to 26.1%. Bulk kraft delignification of mature wood resulted in 5-6% higher yield than juvenile wood from the same clone and the pulping activation energy ranged from 98 $kJ.mol^{-1}$ to 120 $kJ.mol^{-1}$.

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INTRODUCTION

About 60% of the wood harvested from Canadian forests goes into the production of pulp and paper and Canada is the largest producer of newsprint in the world. Forest products form about 17% of all Canadian exports and the competitive position of Canadian Forest Industries (particularly the pulp and paper industry) in the world markets is of vital importance to Canadian economy. This competitive position is largely dependent on the cost of producing pulp and paper in Canada and a significant proportion of the cost is attributable to raw material costs. With the steady depletion and increased cost of long wood fibre resources, the utilization of hardwoods has risen manifold.

The production of biomass from short rotation intensive culture (SRIC) plantations using hybrid willows (Salix spp.) is a relatively new concept. High density plantings of 10,000-100,000 stools have been examined. Since willows resprout following cutting, coppice can be harvested every 1 to 5 years. SRIC employed on sites no longer required or considered suitable for agriculture. This aspect can be of particular value where companies require dependable sources of furnish close to the mill.

A number of hybrid willows from European and Canadian sources are currently being tested in Ontario. Much of this work has focused on improving yields. However, the suitability of this potentially valuable resource for pulping has not been adequately addressed.

The present investigation will, therefore, establish ratings of different hybrid willow (Salix spp.) clones from the standpoint of a pulpwood source and identify superior clones for propagation.

The objectives of this investigation were: (a) to determine morphological characteristics such as fibre length, cell wall thickness and wood density in a range of hybrid willow clones, (b) to determine the chemical compositions such as lignin content in each clone, (c) to characterise the structure of the lignin from each clone and (d) to establish reaction rate constants and Arrhenius activation energy for kraft pulping of the hybrid willow clones and e) to derive these characteristics in willows and to compare them with similar hardwoods.

MATERIALS AND METHODS

The material consisted of shoots of sixteen hybrid willow clones. Out of these, three clones were fourteen years old and were harvested from the Newell Tract forest in

February, 1984. The remaining thirteen clones were 1 and 2 years old and were selected at the stool bed plantation, compartment D6, of the Ontario Ministry of Natural Resources nursery at Midhurst, Ontario in March, 1983. The samples were cut to 20 cm long and stored at −4 °C until ready for use.

All the analyses were carried out on bark-free wood and wherever applicable Tappi standards were followed.

Fibre Length:

For measurement of fibre length and width, the modified Franklin method was used for pulping. The wood pieces were cut into pieces about 20 mm long and 2 mm x 2 mm in cross section. These wood samples were suspended in test tubes containing a solution of equal parts of glacial acetic acid and 30-35% hydrogen peroxide and the test tubes were put in boiling water. Approximately 6.5 hours were required for the wood samples to become uniformly white. Slides were prepared from the dilute fibre suspensions for measurement of fibre length and width (maximum). Twenty measurements were made for each clone and recorded with an Apple II Digitiser Calibrated by Nerniers[1].

Cell Wall Thickness and Lumen Diameter:

Transverse section of the stem from each clone were prepared by using dehydration and infiltration with distilled water and ethanol[1]. Then, the specimen was embedded with Paraplast. A sliding microtome, Spencer model 860, was used for section. Thin sections (<20 μm) were prepared and double stained with safranin and fast green and were mounted in slides for cell wall thickness measurement.

For lumen diameter, samples from the largest lumen diameter near vessels were measured. Random sampling of cell wall thickness from two or three rows of cells near the early wood transition area were measured. Again, twenty measurements were made for each sample.

Specific Gravity:

Basic specific gravity was determined on wood samples from different young clones as well as samples from different growth layers from mature clones, and was based on the principle of maximum moisture a wood sample can attain and on a green volume basis[2]. Three measurements per sample were determined.

Mill Wood Lignin and Klason Lignin:

For the extraction of milled wood lignin, Björkman's[3,4,5] method of grinding wood in toluene, extracting in dioxane and subsequently purifying by successive precipitations was followed.

Soluble lignin content in milled wood lignin was determined by Klason lignin method - treating milled wood lignin with 72% sulphuric acid and measuring UV absorbency at 205 nm on acid filtrate[6]. Three measurements per sample were determined.

^{13}C Nuclear Magnetic Resonance, Ultraviolet Absorbency and Methoxyl Analysis:

The NMR spectra were obtained with a Bruker WM-250 spectrometer controlled by an Aspect 2000A minicomputer. A 8-9% solution of acetylated milled wood lignin in d_6-acetone was used for all experiments[1].

Ultraviolet absorbency measurements on milled wood lignin dissolved in methyl cellulose (ethylene glycol methyl ether) at various concentrations were carried out with a Beckman Model DU single beam spectrophotometer[1].

Methoxyl contents of the milled wood lignin were determined at the Schwarzkopf Microanalytical Laboratory, New York. 2-methoxybenzoic acid was used as a standard[1].

Pulping Kinetics:

The pulping study was carried out in 20 mL stainless steel reactors. The liquor composition was maintained at 32 g/L of active alkali and 25% sulphidity. The wood was ground to 40 mesh and extracted with ethanol-benzene and ethanol for a total of 96 hours. Cooking temperature was maintained at 140 °C, 155 °C and 170 °C for various lengths of time: 15, 30, 60, 90, 180, 240 and 300 minutes. Klason lignin content of the wood and the pulp was determined.

RESULTS AND DISCUSSION

Fibre Morphology:

(i) One and two years old clones: By using analysis of variance[7] and Duncan's multiple range test[8], significant variation in fibre length and cell wall thickness was observed among different clones as shown in Table 1. Based on twenty measurements for each clone, fibre lengths vary from 0.49 mm to 0.70 mm with an average value of 0.59 mm and the coefficient of variance of ± 14.3%. Cell wall thickness ranged from 2.5 μm to 3.6 μm with an average of 2.9 μm ± 0.03% as shown in Figure 1. Clonal ranking based on the ratio of fibre length to cell wall thickness is shown in Figure 2. Since the relative fibre flexibility (fibre to cell wall thickness) is an indication of interfibre contact and bonding of paper, clone SA7 is the most suitable source of pulp because of its high flexibility.

The volumetric composition of fibres of one year old clone is found to be approximately 70% and the rest consisting of vessels and rays. This is higher than that reported for other hardwoods[9]. High fibre fraction in the volumetric composition makes Salix spp. valuable for paper manufacturing. The volumetric composition or fibre fraction in two years old clones were found to be much lower - in the range of 50-55% which seem to be more in line with the published values[10]. Significant variation in size of the vessels were also noticed and perhaps account for such reduction in fibre proportion with a consequent increase in vessel proportion. No account of longitudinal parenchyma was made and this may also reduce the increased proportion of fibres to a certain extent.

The average specific gravity for both one or two years old clones varied between 0.36 to 0.52 with an average of 0.43 ± 12.6%. Since the yield of pulp, expressed as ratio of fibre to a given quality (by mass) of raw material in the form of chips, tends to be a direct function of specific gravity, high specific gravity means more dried matter contained in the volume of chips that can be packed into a digester. Hence, Salix spp. obviously can be a significant source of wood for pulping.

TABLE 1.

Analysis of Variance for Fibre Morphology and Chemical Composition of Hybrid Salix Clones.

Subject	Source of Variation	df Degree of Freedom	SS Sum of Square	MS Mean of Square	F Ratio	F Critical Value*
Fibre Length	Among Groups	10	0.9390	9.39 x 10^{-2}	31.82	1.87
	Within Groups	209	0.6168	2.95 x 10^{-3}		
Cell Wall Thickness	Among Groups	10	3.3271 x 10^{-5}	3.3271 x 10^{-6}	5.13	1.87
	Within Groups	209	1.3559 x 10^{-4}	6.4877 x 10^{-7}		
Specific Gravity	Among Groups	12	0.1211	1.009 x 10^{-2}	47.32	2.15
	Within Groups	26	5.5442 x 10^{-3}	2.1324 x 10^{-4}		
Total Lignin	Among Groups	12	72.7109	6.0592	45.93	2.60
	Within Groups	13	1.7148	0.1319		

* F critical value is based on 95% confidence interval.

(ii) Fourteen years old clones: Fibre length variation by annual growth layer was determined in three fourteen years old clones and was found to range from 0.5 mm in the first growth layer to about 1.1 mm in the last growth layer (11th ring counted at DBH level) as shown in Figure 3. The fibre length seems to be increasing at a faster rate for the first 2-3 years and then the rate increment decreases and finally around 10th and 11th growth layer, the fibres attain about 1 mm in length reflecting the starting of a period of more or less stabilised functioning of the mature cambium.

No noticeable variation in specific gravity was observed in radial as well as vertical direction in the trunk of a tree as shown in Figure 4. The specific gravity variation with height in the tree shows very little consistency and no overall dominance of a single pattern is noticeable. This appears to be partly the result of diversity of cell types in different parts of trees, but may also be the result of varying growth influences.

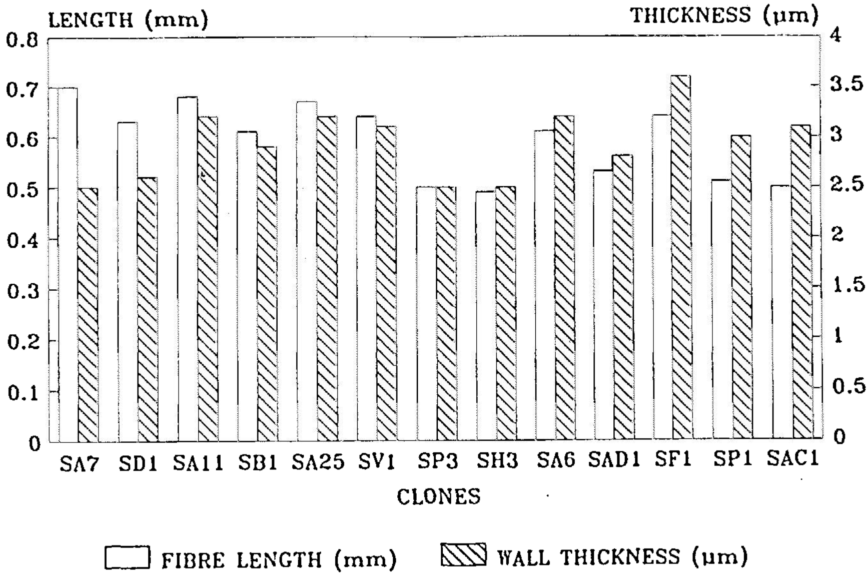

FIGURE 1. Variation of Fibre Length and Cell Wall Thickness of Hybrid Willow (Salix spp.) Clones

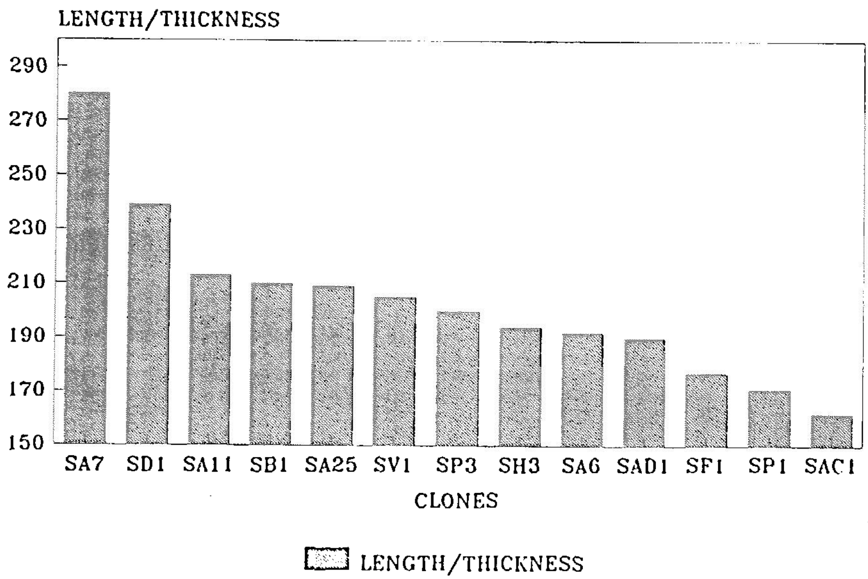

FIGURE 2. Clonal Ranking Based on the Ratio of Fibre Length to Cell Wall Thickness

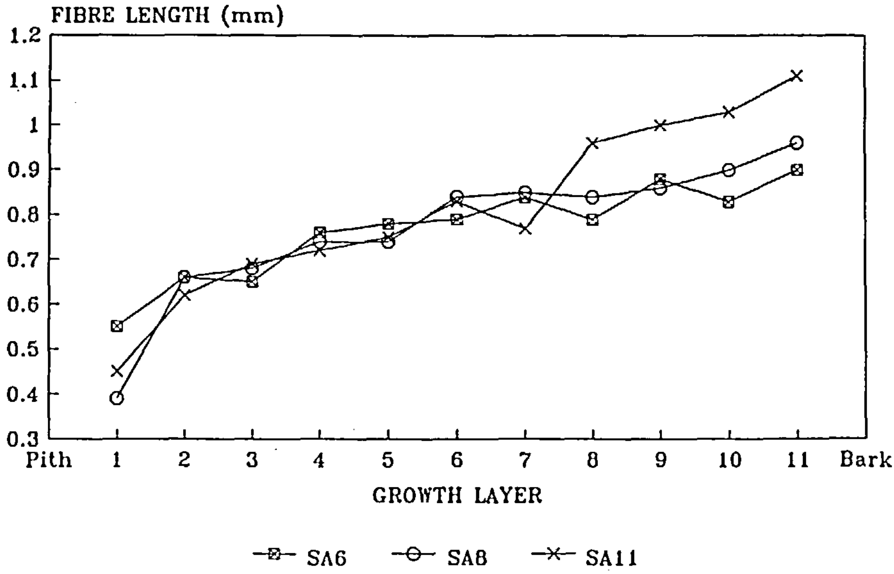

FIGURE 3. Variation of Fibre Length with Age in Hybrid Willow (Salix spp.) Clones

One of the three clones, SA11, indicates higher specific gravity (0.37) than the other two (0.35). The weighed average fibre length of this clone (calculated based on the total clone volume) after 11 years is 0.87 mm ± 23%, this clone seems to be a superior clone compared to the other two fourteen years old clones (SA6 and SA8). The clone SA6 has slightly shorter fibre but higher cell wall thickness.

Table 2 shows the comparison of morphological properties of hybrid Salix spp. clones with other hardwood and softwood species. Salix spp. has lower average values of specific gravity, fibre length and cell wall thickness than the corresponding literature values of hardwood and softwood species[11,12]. However, clonal difference among different Salix clones allows choosing superior clones which display the maximum value of these properties.

Chemical Composition:

Based on extractive-free wood. the Klason lignin content of wood from different

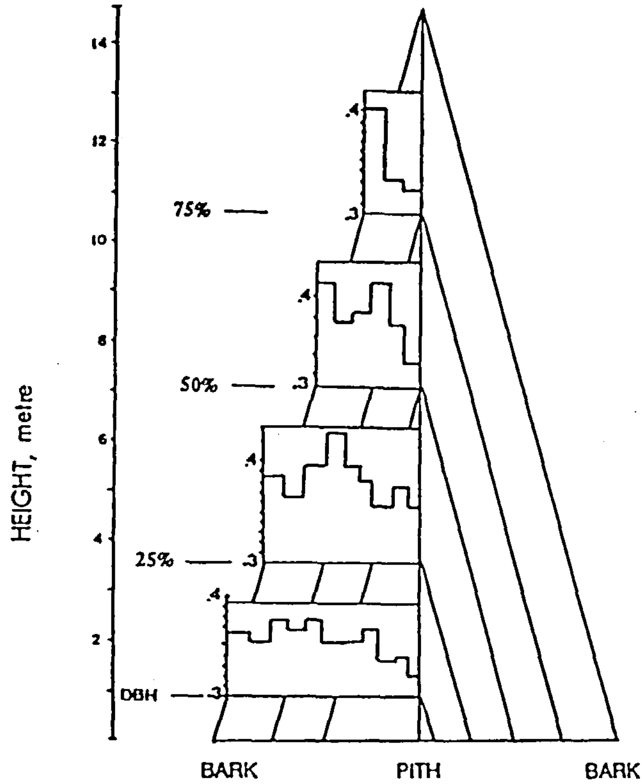

FIGURE 4. Variation of Specific Gravity in Radial and Vertical Direction in the Trunk of a Tree

tissues. The average Klason lignin content is 23.38% with the coefficient of variance of ± 7.38%. The fourteen years old woody tissues indicate lower lignin content of 19.58% ± 1.71% as shown in Table 3.

Soluble lignin content in hybrid willow clones was found to be 2.23% ± 2.2% on extractive-free wood or about 8-9% on Klason lignin. This is identical to the reported values for similar hardwoods[13]. Examination of chlorite holocellulose preparation indicated that the presence of more than 100% undetermined acid-soluble lignin. Also the interference with this estimate by furan-type compounds, formed mainly during the refluxing step in the lignin determination, could be decreased significantly by simply boiling in 3% sulphuric acid instead of refluxing[6].

TABLE 2.

A Comparison of Morphological Properties of Hybrid Salix Clones with Other Hardwood and Softwood Species.

SPECIES	PROPERTIES		
	SPECIFIC GRAVITY	FIBRE LENGTH (mm)	CELL WALL THICKNESS (μm)
Hardwoods[11]			
Red alder	0.38	1.25	3.54
Aspen	0.39	1.05	3.20
Sweetgum	0.45	1.65	6.40
American elm	0.50	1.35	4.20
Paper Birch	0.53	1.51	3.75
Average	0.45	1.36	4.22
Softwoods[12]			
Lodgepole pine	0.43	3.45	3.02
Western larch	0.53	3.96	3.87
Douglas fir	0.46	3.50	3.41
Western hemlock	0.45	3.39	3.23
Sitka spruce	0.34	3.19	2.87
Average	0.44	3.50	3.28
Salix spp.			
1-2 years old	0.43	0.59	2.90
14 years old	0.37	0.86	----

Although lignin structure influences the chemical and the physical behaviour of wood during pulping and the use of resulting fibres, no widely accepted description of the lignin in hardwoods has been presented. Whereas softwood lignin are composed of mainly guaiacyl phenylpropanoid units (derived from coniferyl alcohol and have one methoxyl substituent on the aromatic ring), hardwood lignin additionally contains significant amounts of syringyl phenylpropanoid units (derived from sinapyl alcohol and have two methoxyl substituents on the aromatic ring).

TABLE 3.

Klason & Soluble Lignin in Different Clones (Based Percent Extractive-Free Wood)

CLONE		KLASON LIGNIN		SOLUBLE LIGNIN	
		AVERAGE	STD. DEV.	AVERAGE	STD. DEV.
SV1	1 YR.	20.84	0.30	2.32	0.03
SAC1	1 YR.	22.50	0.20	2.20	0.08
SD1	1 YR.	23.84	0.54	2.24	0.02
SB1	1 YR.	24.25	0.33	2.23	0.04
SAD1	1 YR.	24.77	0.11	2.32	0.04
SP3	1 YR.	24.51	0.11	2.17	0.01
SA6	1 YR.	25.13	0.21	2.21	0.01
SP1	1 YR.	26.12	0.59	2.21	0.01
SA11	2 YR.	19.78	0.51	2.28	0.02
SA7	2 YR.	22.07	0.46	2.26	0.00
SH3	2 YR.	23.07	0.45	2.26	0.03
SF1	2 YR.	23.72	0.20	2.13	0.02
SA8	14 YR.	19.34	0.40	2.31	0.00
SA6	14 YR.	19.82	0.17	2.23	0.03

Carbon-13 nuclear magnetic resonance, ultraviolet absorbency, methoxyl analysis, and molecular weight distribution of milled wood lignin isolated from different hybrid willow clones are at present carried out to further determine the nature of lignin in hybrid willow. Because ^{13}C-NMR spectroscopy of mill wood lignin has been shown to differentiate between hardwood and softwood lignin[14] it seemed likely that ^{13}C-NMR could provide a useful tool to investigate the differences, in the chemical structure of these lignin types among clones.

Standard absorptivities of milled wood lignin extracted from different clones were calculated by measuring absorbency at 278 nm. The peak shifted towards lower wavelength from 280 nm indicating the presence of syringyl lignin, as expected for hardwood lignin[15]. The extinction coefficients vary from 12.17 to 14.31 $L.g^{-1}cm^{-1}$ (average 13.72 ± 0.72) while the quoted figure for poplar is 14.2 $L.g^{-1}cm^{-1}$ run in methoxyethanol.

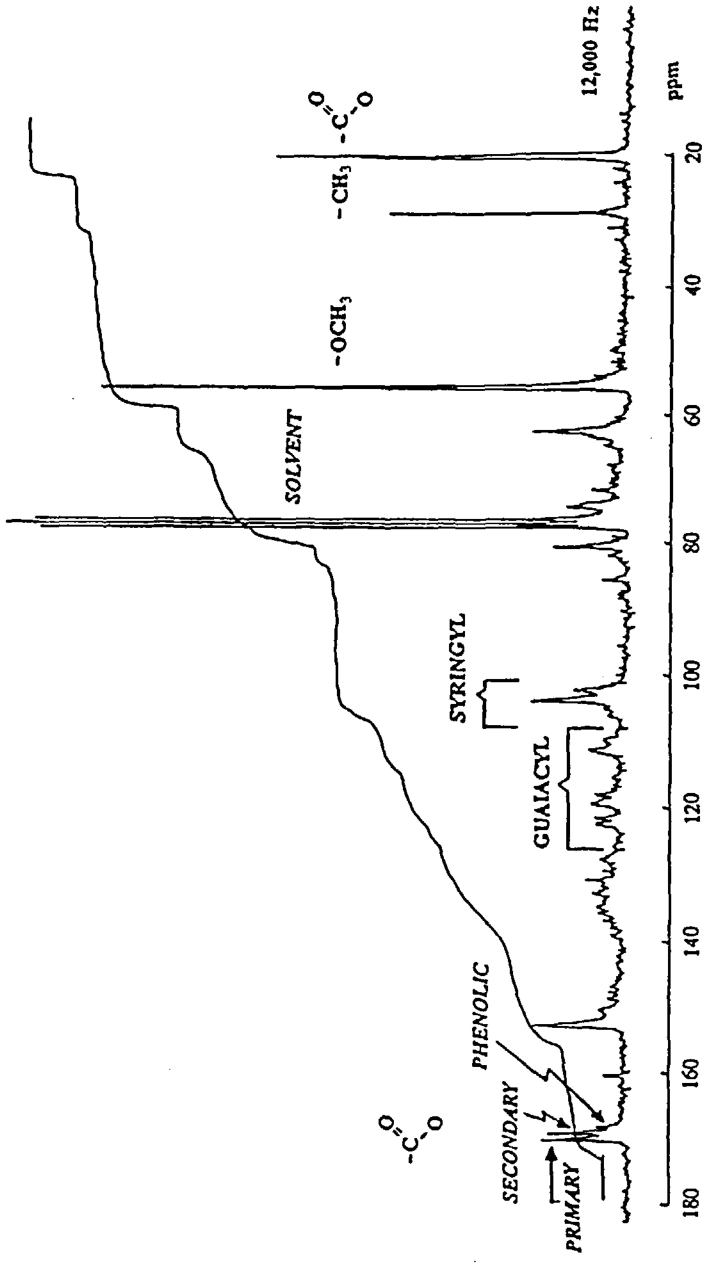

FIGURE 5. ^{13}C NMR Spectrum of Acetylated MWL from Hybrid Willow (SA7) Clone

^{13}C-NMR acetylation of the lignin was carried out for 48 hours with acetic anhydride to pyridine ratio of 1 to 1. The acetylated samples were recovered by precipitation in diethyl ether, purification by successive washing with solvent and freeze dried.

^{13}C-NMR of acetylated milled wood lignin led to the conclusion that milled wood lignin extracted from hybrid willow (Salix spp.) are heterogenous in their syringyl to guaiacyl composition[16]. The syringyl to guaiacyl ratio for one of the hybrid willow clone (SA7) was calculated to be 0.625 as shown in Figure 5. The syringyl content of the typical total hardwood lignin content varies between 20% and 60%[15].

Initial results from acetylated milled wood lignin from hybrid willow (Salix spp.) clones indicate wide variations in the aliphatic portions of the phenylpropane units which have brought a basic question - are such variations caused during milling process?

To determine this, solid state ^{13}C-NMR was run on extractive-free wood for different clones. Preliminary analysis indicates variations in lignin chemical structure. However, as these spectra are composed of hemicellulose and cellulose also, it becomes important to superimpose the cellulose and hemicellulose spectra and thereby look at the spectra of lignin only as it exists in wood. This possibility is being explored[17].

Delignification:

Normally, hardwoods will be preferred for corrugating medium for which neutral sulfite semichemical process is the prevalent pulping process. However, this study is to look at the delignification kinetics or rate constants for which kraft pulping is the ideal process.

In comparing the yields of pulps from mature wood and juvenile wood of hybrid willow (Salix spp.), it is observed that mature wood gives about 5-6% higher yield than the corresponding juvenile wood from the identical clone[18]. This is due to higher amounts of hemicelluloses in young wood compared to mature wood. Wood, Ahlgren and Goring[19] observed that hemicellulose govern the pore size in the cell wall and thus the rate of delignification. These hemicelluloses are known to be dissolved early in the cook. Removal of hemicelluloses increases the pore size and therefore also increases the rate of delignification. However, once such hemicelluloses are removed from the wood early in the cook, the delignification rate remains more or less the same for young as well as mature clones. Therefore, in predicting the expected yield from young clones, a 5-6% lower yield also needs to be considered. The activation energy for bulk delignification ranged from 98 $kJ.mol^{-1}$ to 120 $kJ.mol^{-1}$ with an average of 107 $kJ.mol^{-1}$ ± 6.5%. This is less than the reported value of 132 $kJ.mol^{-1}$ for species such as Eucalyptus regnans[20].

CONCLUSIONS

1. Hybrid willow (Salix spp.) is an alternative choice of wood for pulp production based on its physical morphology, chemical composition and delignification characteristics.

2. The maximum fibre length growth rate for hybrid willow (Salix spp.) clones is in the first two to three years and the average fibre length for one and two years old clones are 0.59 mm.

3. The average cell wall thickness and specific gravity for one and two years old clones are 2.9 μm and 0.43 respectively.

4. *Both syringyl and guaiacyl lignin are present in hybrid willow (Salix spp.) lignin as* evidenced by ^{13}C-NMR and the average Klason lignin content is 23.38%.

5. Pulping of mature wood results in 5-6% higher yield than juvenile wood from the same clone with the average bulk delignification activation energy of 107 $kJ.mol^{-1}$.

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