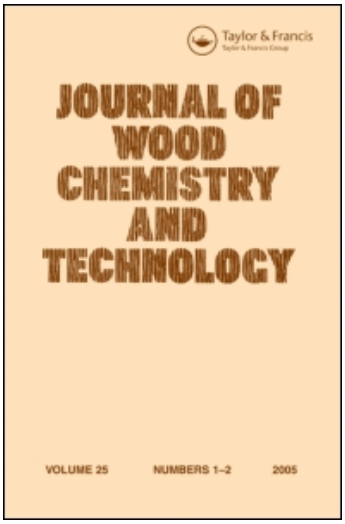

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CHEMISTRY AND DELIGNIFICATION KINETICS OF CANADIAN INDUSTRIAL HEMP (*Cannabis sativa* L.)

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ABSTRACT

Strategies to diversify the Canadian fibre supply have provided an impetus for investigating a wide variety of alternative fibres including industrial hemp (Cannabis sativa L.) in Canada. The alkaline delignification kinetics of Canadian hemp (bast, core and whole stem fractions), using micro pulping units was investigated. The nature of hemp (macromolecule proportions) was a major contributor to the chemical pulping behaviour shown in the results. The initial lignin and holocellulose content of the bast were 10% and 85%, respectively, and the core lignin and holocellulose contents were 21% and 72%, respectively. The bast fibre had a comparative pulping advantage over the core fibre region due to its chemical constitution. The activation energies for lignin removal from hemp are 41 kJ/mol, 76 kJ/mol and 76 kJ/mol for the bast, core and whole stem respectively. These are considerably lower than the reported values for traditional wood pulp species.

INTRODUCTION

It is becoming widely recognized that both the land and its resources are finite; forest area is decreasing around the world. Both the forest industry and the public have started to raise concerns over where raw material is going to come from to sustain the manufacturers of sawn timber, wood-based panels and pulp and paper products. Vigorous regeneration regimes, improved production efficiency of forest stands and systematic reductions in annual allowable cuts have become the norm in order to address the forecasted global fibre supply shortage in the future. Efforts to increase fibre supply have promoted research into alternative fibre resources, such as agricultural residues and non-wood plants. Ultimately, it is the diversification of our fibre supply that will ensure that resource constraints are met and that environmental restoration strategies are successfully implemented.

In nations where tree species are not the predominant source of fibre, there has been much research dedicated to the development of processes and technologies for non-wood plant species. The use of non-wood plants as a raw material source for mechanical pulping has been investigated.[1,2] Research on novel chemical processes such as organosolv pulping of non-wood fibre are well documented.[3–6] Both the soda and kraft pulping of non-wood fibre has also been studied.[7–11] The chemical and morphological characteristics of non-wood species are highly variable between species as well as within species classes. Part of this variability can be explained by specific agronomic conditions that the plants are subjected to. Thus, acquiring knowledge of specific non-woods grown in one's nation is of great importance when determining potential end uses for the fibre resource.

This study was initiated to assess the suitability of Canadian-grown hemp fibres for use in the national pulp and paper sector. To achieve this objective, the delignification kinetics of hemp fibre was studied through a series of laboratory scale micro-pulping experiments. The preliminary results of this study were previously published.[12]

EXPERIMENTAL

The raw material used in this research study was hemp (*Cannabis sativa* L.) fibre which was grown and donated by Hempline Inc. (located in southwestern Ontario, near the city of London). Hemp is a non-wood plant fibre. This annual plant grows from seed each year to an average height of 2.5 m. As shown in previous work,[13] hemp fibre has different

physical and chemical features depending on from which lateral portion of the stem it was derived. For these reasons, the bast, core and whole stem portion were studied.

To begin, the fibre was air dried and ground in a Wiley mill to pass a 0.4 mm screen and then extracted with solvents to remove extractives that could consume the white liquor during the pulping process. Extraction was carried out according to Tappi standard test methods T257 cm-85 and T264 om-82 respectively. Extracting the hemp fibre prior to the laboratory micro-pulping tests provides a baseline for comparison with other wood species. Usually, hemp is field retted and the period of retting varies according to the grower and climatic conditions. Thus, extracting the fibre will eliminate the variable extractives content due to the different degrees of retting. If the fibre were not extracted, these low molecular weight molecules would be dissolved in the pulping liquor, thereby reducing the active alkali available for delignification. Depending on the concentration of extractives in the hemp, from 3–6% of lignin would not be reacted and removed. It is understood that in a commercial setting, pre-extraction will not take place. However, the focus of this work is to investigate the lignin complex during alkaline pulping and in a laboratory setting and extracting the fibre was a useful means of eliminating the extractives variable. Chemical pulping of hemp was carried out in 25-mL stainless steel reactors. Into each reactor, 2.0 g on oven dry basis extractive-free fibre and 12 mL of pulping liquor were measured. The pulping liquors were made to have an active alkali (AA) of 15% and 18% as Na_2O from NaOH. The fibre to liquor ratio was 1:6. This liquor to fibre ratio was chosen based on previous chemical pulping work with wood and non-wood species.[12–19] The delignification of the hemp was followed at various cooking temperatures (set points) and residence times (i.e. $T = 170$, 160, 150, and 140°C and $t = 210$, 180, 150, 120, 90, 60, and 30 min.). For each time-temperature series, five replicates were produced. The setup of the apparatus included a large vessel with 3 L of silicone oil, an electric mixer to stir the hot oil, two hotplates, bar and hooks for reactors and a manual thermo-regulator.

The temperature of the oil was always raised 3°C above the desired temperature to allow for the temperature decrease once the reactors were initially immersed in the oil. Once the reactors had equilibrated to the desired temperature, the fibre was cooked for the designated time at the set point. At the end of the cook, the reactors were quenched in cold water. The pulp was thoroughly washed with distilled water once removed from the reactor. Two samples were oven dried for pulp yield determination and three samples were air-dried for chemical characterization; lignin

(T222 om-88 and T250 um-94), holocellulose[20] and α-cellulose (T203 om-93) determination.

RESULTS AND DISCUSSION

Hemp Characterization

Figure 1 shows a picture of a cross section of a hemp stem depicting the various areas of the stem.

As demonstrated in Figure 1, the core region constitutes the greatest fraction of the stem while the bast region is the smallest. The density of the pith tissue is the lowest, followed by the core with a slightly higher density and finally, the bast tissue has the highest density relative to the other tissue regions. The difference in density between the core and the bast regions of the stem is clearly evident in the SEM micrograph shown in Figure 2.

This micrograph shows the transverse, radial and tangential surfaces of the bast portion of the stem, while only the transverse and radial surfaces are visible for the core. Three types of cells were evident in both bast and core, while only one cell type was visible in the pith. In the bast, there were long cells similar to fibre tracheids, shorter cells analogous to sieve tubes and shorter irregular cells similar to parenchyma cells. The fibre tracheids in the bast were extremely long, and had thick cell walls and simple pits along the length of the cells. The differences in the cell wall thickness between the core and the bast regions of the stem are also visible in Figure 2.

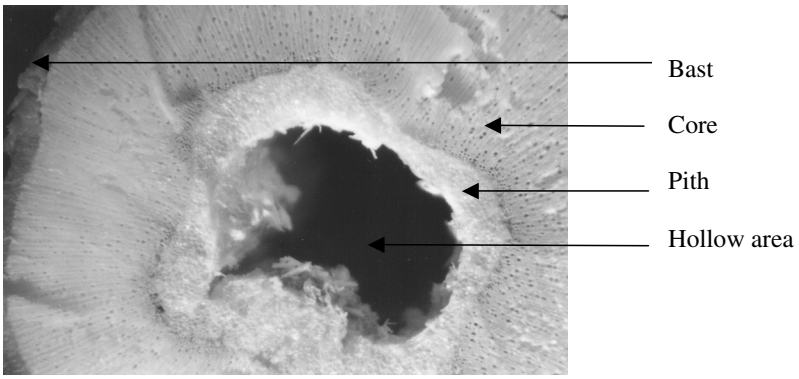

Figure 1. Cross Section of a Canadian Hemp stem −10 × mag.

In addition to the different physical features, hemp also has different chemical composition throughout the different tissue regions of the stem. Table 1 summarizes the chemical composition of hemp according to the major tissue regions.

The greatest amount of extractives was found in the core fibre as opposed to the bast region. This is characteristic of other non-wood plant fibres.[19] The measure of extractives is important because it has a negative effect in chemical pulping processes; fibres with high extractive contents are poorly pulped because the extractives consume a portion of the pulping liquor. The bast is characterized with a high holocellulose content, of which alphacellulose comprises over two-thirds. In general, a higher alpha-cellulose content will enable the bast fibre to have a competitive advantage

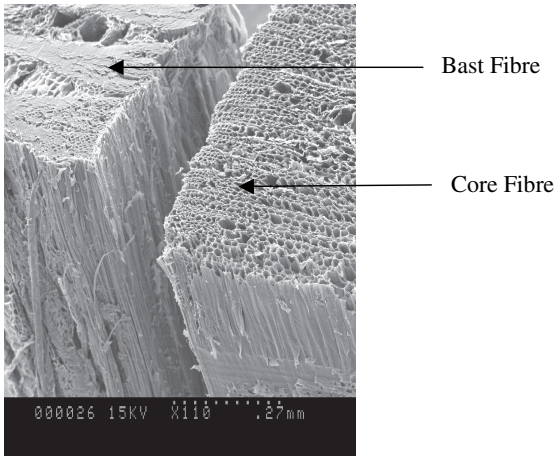

Figure 2. SEM micrograph of hemp bast and core fibre.

Table 1. Hemp Chemical Fractionation

	% Total Mass, n = 30				
	Extractives	Holocellulose	α-cellulose	Lignin	Ash
Bast	3.02 ± 0.42	84.8 ± 1.78	60.6 ± 2.64	10.0 ± 1.96	2.17 ± 0.07
Core	5.60 ± 0.32	72.3 ± 3.23	33.4 ± 0.76	21.2 ± 1.14	0.90 ± 0.09
Whole Stem	3.77 ± 0.38	77.9 ± 2.44	43.0 ± 1.07	15.2 ± 0.58	3.18 ± 0.67

Mean values ± standard deviation

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over the core; bast fibre will produce higher pulp yields and impart greater strength properties. The core fibre also has a high hemicellulose content; raw materials with high hemicellulose contents generally produce pulps with a lower yield. The higher lignin content in the core fibre will consume greater quantities of white liquor during the chemical pulping process. The ash content of the bast fibre is 1% greater than the ash content of the core fibre; this may be a direct result of field retting which may increase the silica content of the hemp stem surface area by surface contamination. The other chemical components may also be affected by field retting; retting decreases the amount of extractives present in the fibre. In this case, if the content of one of the chemical components decreases, the fractional value of the others will increase; this does not mean that the other component have had an increase, rather the mass distribution has changed.

Delignification Study

For each pulp sample prepared, the yield, lignin, holocellulose and alphacellulose contents were measured. Using these data, the optimum pulping conditions were determined by comparing the following criteria:

1. minimal residual lignin content
2. maximum pulp yield
3. maximum alphacellulose

Although Criterion 1 works in contradiction to the other two criteria, it was the most heavily weighted in this comparison; greater removal of lignin will enhance the optical properties of the pulp and also reduce the amount of inputs needed to brighten the pulp at a later stage of the manufacturing process. Using the listed criteria, the data set was sorted and the most desirable pulps are listed in Table 2.

The results in Table 2 clearly show that, at both chemical treatments, the core fibre was the most difficult to delignify (i.e. higher residual lignin contents); conversely, the lignin in the bast fibre was more readily removed. It is also important to note that the bast fibre retained the highest alphacellulose content in both of the treatments.

In Figure 3, the selectivity of the stem fractions are compared; raw materials with favourable pulp selectivities exhibit pulps with high yields and low residual lignin contents. In this case, the most selective fibre region are those that have the greatest slope as shown by the bast portion of the hemp fibre. For any given residual lignin content, the bast exhibits the greatest pulp yield. The least selective of the hemp stem is the

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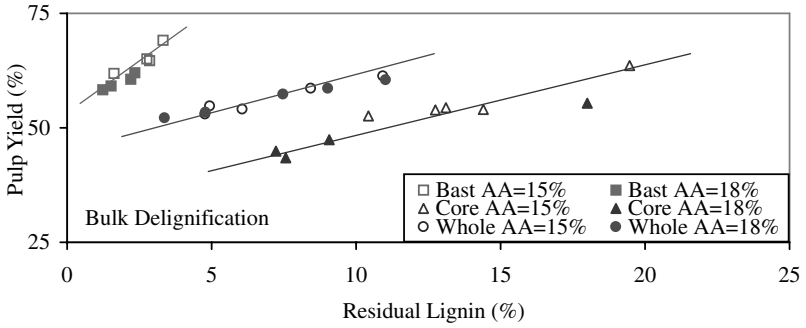
Table 2. Time/Temperature Pulp Optimization Summary

AA(%)		Temp. (°C)	Time (min.)	(%), n = 2 Residual Lignin[a]	Pulp Yield	α-cellulose[a]
15	Bast	160	210	0.68 ± 0.17	61.2 ± 0.27	76.6 ± 2.69
	Core	170	120	10.1 ± 0.47	54.6 ± 4.37	58.1 ± 0.18
	Whole	170	150	4.54 ± 0.72	53.5 ± 0.09	69.6 ± 1.18
18	Bast	170	150	1.15 ± 0.25	59.9 ± 0.33	79.0 ± 3.10
	Core	170	180	6.14 ± 0.27	46.6 ± 0.35	63.8 ± 0.27
	Whole	170	180	3.37 ± 0.14	52.2 ± 0.51	65.7 ± 0.81

[a]based on O.D. pulp, mean values ± standard deviation



Bast, y = 4.512x + 52.555, r = 0.930
Core, y = 1.319x + 35.762, r = 0.931
Whole, y = 1.193x + 47.918, r = 0.981

Figure 3. Hemp Pulping Selectivity (based on residual lignin content). Significance of correlation at a confidence level of 95%.

core component, where high residual lignin contents are complemented by low pulp yields. The low lignin removal and greater yield losses were caused by the less reactive core lignin as compared to that of the bast. The whole stem fraction has a selectivity intermediate to the bast and the core. In addition, there is little difference between the two active alkali treatments used; the points on the plot are in very close proximity to one another.

Pulp yield is not only dependent on the lignin removal but also on the degree of disintegration of the carbohydrate fraction during the pulping process. The following Figures 4, 5, and 6 demonstrate the relative changes

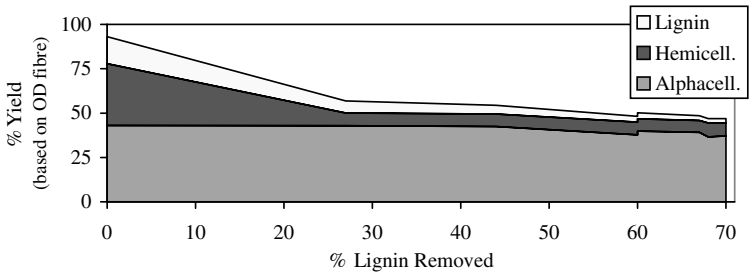


Figure 4. Whole Stem Component Change during Pulping.

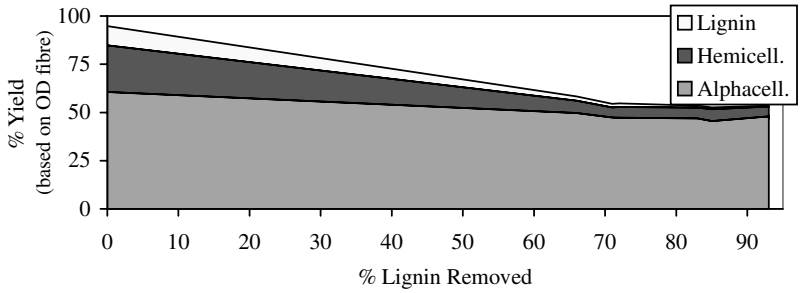


Figure 5. Bast Component Change during Pulping.

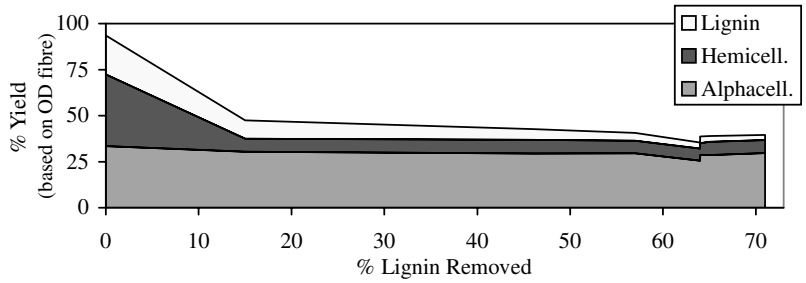


Figure 6. Core Component Change during Pulping.

of alphacellulose, hemicellulose and lignin contents during the pulping process. Each of the figures is expressed as a function of percentage lignin removed.

Figures 4, 5, and 6 all show that the greatest reduction occurred in the hemicellulose component, while the alphacellulose contents remained relatively unchanged throughout the pulping. The core fibre exhibited

a reduction in the hemicellulose content early in the pulping process (i.e. at 15% lignin removed, there had been a dramatic decrease in hemicellulose content). Core fibre also shows a very slow removal of lignin; again showing the degree of difficulty experienced when pulping the core fibre. The difficulty experienced in pulping the core fibre may partly result from the higher degree of lignification of the core fibre in comparison to the bast fibre. The core lignin structure may also be different from the bast, thus the different lignin removals were exhibited. In the case of the bast fibre, there was a consistent reduction of lignin and a gradual removal of hemicellulose (i.e. until 70% lignin removed). In general, upon completion of the pulping, there were only 25% of the original hemicellulose content left in the hemp fibre. The removal of hemicellulose was large due to the structural nature of the polymer (i.e. it is a branched, carbohydrate structure having a lower molecular weight and a greater number of reaction sites than cellulose).

The chemical kinetics of alkaline pulping processes have been studied at length as demonstrated by the body of literature available.[21–30] Thus, it is known that alkaline pulping is a first order reaction and that the rate of change of lignin removed per unit mass of fibre is related to the product of the amount of lignin remaining in the fibre and the concentration of sodium hydroxide and sodium hydrosulfide in the liquor (in this study only sodium hydroxide was used – soda pulping). This relationship may be expressed as follows:

$$-dL/dt = k \cdot L \tag{1}$$

where dL/dt = lignin removal rate
k = chemical reaction rate constant
L = residual lignin in the pulp

The chemical reaction rate constant, k, is related to temperature by the Arrhenius law which is:

$$k = A \exp^{-Ea/RT} \tag{2}$$

where A = Arrhenius constant
E_a = activation energy
R = gas constant = 8.314 kJ/°K·mole
T = absolute temperature (°K) [25]

Integration of Equation 1 shows that there is a straight line relationship between the natural logarithm of the residual lignin content and the cooking time of the pulp. From the pulping data collected, the logarithmic plots of percent residual lignin (based on oven dry fibre) against cooking

time (i.e. pulping time) for the three different fibre groups were produced. Figure 7 shows the logarithmic for the whole stem fraction.

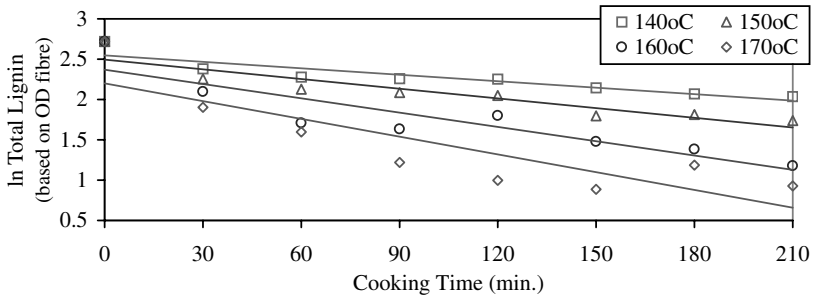
Similar to Figure 7, the plots for bast and core each show a negative trend with increasing pulping time. With increasing temperatures, the reaction proceeded more rapidly as shown by the increase in the slopes of the trend lines. Integration of Equation 2 yields:

$$\ln k_O = \ln A - E_a/R \cdot 1/T \quad (3)$$

The slope of the straight line ($-E_a/R$) is obtained by plotting $\ln k_O$ versus $1/T$; using the slope, the activation energy was calculated. Figure 8 shows Arrhenius plots of $\ln k_O$ versus $1/T$.

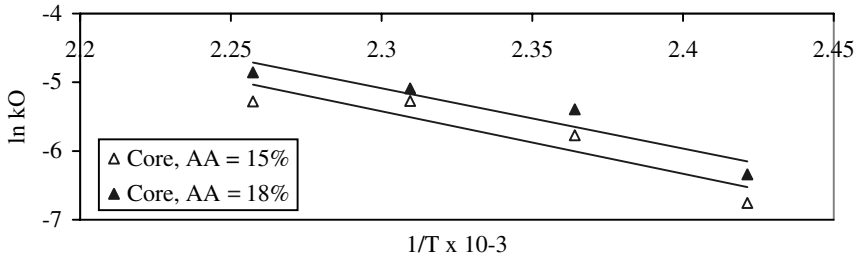
The activation energies for the core, bast and whole pulps were calculated using the slope of these plots as described earlier. The activation energies are listed in Table 3.

The calculated activation energies shown in Table 3 clearly indicate that the bast fibre portion is considerably more suited for pulping as it requires a lower quantity of energy to induce the chemical reaction. The activation energies for kenaf have been reported to be 68 kJ/mol for bast, 91 kJ/mol for core and 75 kJ/mol for whole.[19] These figures indicate that hemp fibre has a slight advantage over kenaf with respect to the required activation energy for bulk delignification. The chemical removal of lignin from a fibrous material has been classified into three distinct stages: initial, bulk, and residual delignification.[24] Typically, the initial delignification stage is characterized by very quick lignin removal. The carbohydrate



140°C, y = -0.002x + 2.426, r = 0.976
150°C, y = -0.003x + 2.335, r = 0.965
160°C, y = -0.004x + 2.121, r = 0.917
170°C, y = -0.005x + 1.823, r = 0.835

Figure 7. Logarithmic plots for soda pulping of hemp whole stem fibre. Significance of correlation at a confidence level of 95%.



Core, AA=15%, y = -9.096x + 15.499, r = 0.920
Core, AA=18%, y = -8.770x + 15.085, r = 0.949

Figure 8. Arrhenius plot of soda hemp core fibre. Significance of correlation at a confidence level of 95%.

Table 3. Calculated Activation Energies

		Activation Energy (kJ/mol)
AA = 15%	Bast	41
	Core	76
	Whole	76

fraction of the raw material is reduced rapidly in this stage. This decrease is clearly evident in Figures 4, 5, and 6. In each of the stem regions a high proportion of the hemicellulose component is dissolved in the initial delignification stage of pulping. The bulk delignification stage is generally, the longest and it is here that the majority of the lignin is removed. In this stage, the carbohydrate fraction is not affected to the same extent as it is in the initial stage. The residual delignification stage is characterized by very slow removal of lignin.

Subtracting the effective initial lignin, L_{OH}, from the measured lignin content of the raw fibre yields a measure for the rapid initial delignification, L_R, such that:

$$L_F - L_{OH} = L_R \tag{4}$$

where L_F = total lignin content of raw fibre
L_{OH} = effective initial lignin during bulk delignification
L_R = rapid initial delignification[19]

Table 4 summarizes the amounts of lignin removed during the first two phases of delignification.

Table 4 shows the variation exhibited by the stem regions with respect to the efficiency of lignin removal in the initial and bulk delignification stages. These data show that even though the lignin removed in the initial stage is about the same for all stem regions, its proportion to total lignin is greater in the bast tissue than in the core tissue.

Figure 9 outlines the differences in the delignification reaction according to the fibre region. Clearly, in the bast fraction, there is a greater proportion of lignin removed in the initial delignification phase (i.e. close to 65% of the total lignin is removed in this phase). Conversely, the core fraction exhibits greater lignin removal in the bulk delignification phase of the reaction. The whole stem fraction is intermediate between the two delignification phases. The amount of lignin removed in each of the stages is affected by the type of lignin present and not by the active alkali concentration. Thus the data in Figure 9 clearly indicate that the bast lignin is different from the core lignin in its reactivity towards delignification by alkali process.

Table 4. Lignin Removed in Initial & Bulk Delignification Stages

	% Total Lignin, L_F	% Effective Initial Lignin, L_{OH}	% Rapid Initial Lignin, L_R
Bast	10.0	3.76	6.28
Core	21.2	15.2	5.97
Whole	15.2	9.50	5.67

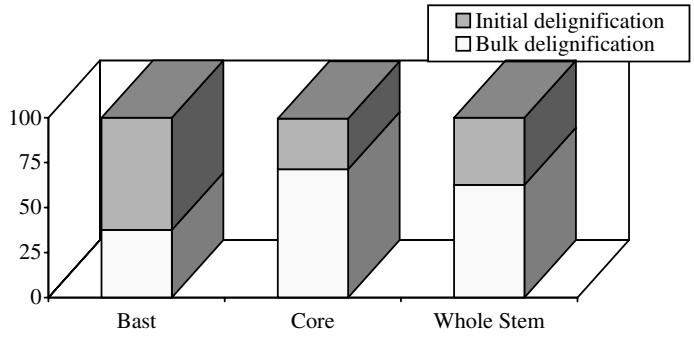


Figure 9. Initial and Bulk Lignin Removal Distribution of Hemp Soda Pulp.

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Although wood species and non-wood species have a different growing cycle, wood species are used as a basis of comparison in Table 5. In so doing, it is apparent that the physical characteristics of hemp core fibre are very similar to those of hardwood species and that the bast fibres are considerably longer than those of softwoods. Chemically, the bast has a greater proportion of holocellulose (with the majority being alpha-cellulose) compared to both the softwood and hardwood data presented. The bast also has considerably less lignin that the softwood and hardwoods. Since a pulp with a high cellulose content and a low lignin content is depicted as being desirable, bast pulp would be suitable for this category. The pulping data also show that hemp is slightly easier to delignify as compared to both the hardwood and softwood as evidenced by the activation energies of each. Although the value of black spruce fibre in Canada will always be higher than any other fibre, it is interesting to see new fibre resources emerging that may be able to compete with it. Effectively developed, these new fibre sources may be suited for limited volume, value added products that could command a higher price in the market such as "tree-free" paper.

Table 5. Comparison of Physical, Chemical, and Pulping Characteristics

	Hemp				
	Bast	Core	Whole	Softwood	Hardwood
Physical Characters					
Cell length (mm)	25.0[13]	0.80[13]	–	3.5[31]	0.80[32]
Cell diameter (mm)	0.04[13]	0.04[13]	–	0.03[31]	0.03[32]
Aspect Ratio	625[13]	20[13]	–	117	26.7
Chemical Constituents					
Extractives	3.02	5.60	3.77	2.2–4.86[31]	2.31–11.87[32]
Holocellulose	84.8	72.3	77.9	71.7[31]	72.3–78.6[32]
α-cellulose	60.6	33.4	43.0	45.6–51.5[31]	41.9–46.8[32]
Lignin	10.0	21.2	15.2	27.3–28.0[31]	20.3–21.8[32]
Ash	2.17	0.90	3.18	0.21–0.36[31]	0.32–0.84[32]
Pulping Parameters					
% AA	15	15	15	≈17–18	≈14
% Sulfidity	0	0	0	25[28–29]	20–30[21,27]
Time (min.)	210	120	150	100[28–29]	100–150[21,27]
Temp. (°C)	160	170	170	165–170[28–29]	150–170[21,27]
Activation Energy (kJ/mol)	41	76	76	125–145[28–29]	125–132[21,27]

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CONCLUSIONS

This work demonstrates that hemp has favourable chemical, physical and pulping characteristics. The fractions of extractives, lignin, hemicellulose, alphacellulose and ash are different in the core and bast region of the stem. When compared to traditional Canadian wood species, hemp has a reduced total lignin content; this lower lignin content allows faster pulping of the raw material. The calculated activation energies for hemp also show that the reaction is more energy efficient as compared to other wood species.

Comparing the bast and the core fibre regions, it was found that, in all cases, the bast fraction was easier to pulp than the core fraction. At an active alkali of 15%, the bast fibre imparted a pulp with high yield and minimal residual lignin. The whole stem was comprised mostly of core fibre (i.e. 50%) and, as expected, its qualities proved to be intermediate between the two fractions.

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