

A diffusion model for the impregnation of lignocellulosic materials

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UNIFORM IMPREGNATION OF lignocellulosic materials prior to any thermal treatments is essential to ensure a homogeneous distribution of the reactive agents throughout the matrix. With a homogeneous distribution of reagents, the kinetics of the desired reactions will also be uniform throughout the system, and the targeted products can be obtained with increased selectivity. This strategy is common to a variety of processes applied to the conversion of lignocellulosic materials. Thus, steam prehydrolysis, all chemical pulping processes, destructuring via steam explosion, and hydrolysis, solvolysis, and pyrolysis (when catalysts are used for the primary thermal decomposition) require adequate control of the impregnation step to “direct the reacting system” toward end products in a uniform manner through the lignocellulosic (wood substrates, straws, plants, and residues) matrix.

In this paper, we present experimental and theoretical evidence for a diffusion mechanism that adequately describes the impregnation of chemicals (NaOH is used as prototype chemical) from aqueous solution. In the following discussion, we describe the rationale for the work, the methods, the results, and the diffusion model.

The case for impregnation can be best understood by considering chemical pulping of chips in the presence of NaOH. In conventional pulping, presteamed wood chips, at a typical liquid/solids ratio of 10

(wt./wt.), are exposed to the “cooking” environment for relatively long times, 1–4 h, at temperatures of up to 180°C (1). Progressive impregnation of NaOH into the matrix takes place and, since hydrolytic reactions are kinetically slow at the “cooking” temperatures, any released acids can be adequately neutralized by the large amounts of NaOH present in the excess liquid phase. This prevents degradation of the cellulose.

In “rapid cooking” processes, such as “steam explosion treatments” at >200°C, the aim is to increase reactor productivity by working at short reaction (i.e., “cooking”) times, typically 2–4 min. The reactive agent (NaOH is our prototype) must be uniformly distributed throughout the matrix prior to steam treatment. Adequate impregnation is thus essential, since the kinetics of hydrolysis in high-temperature treatments are considerable faster than at the lower temperatures used in conventional processes. Moreover, there is no large liquid reservoir of reactive agent, since the major advantage of rapid steam treatments is the low liquid/solid ratio used, not exceeding 3 (wt./wt.), even with the added steam included. Clearly, impregnation prior to rapid steam treatment is necessary if “uniform cooking” is desired.

BACKGROUND

To achieve uniform impregnation experimentally, an understanding of how the liquid phase “moves” through the matrix is essential prior to model development. We thus will

ABSTRACT

Chip impregnation is essential to achieve a uniform distribution of active chemicals throughout the wood matrix prior to rapid pulping. To determine the rate at which chemicals penetrate the wood chips through the radial and axial directions, an impregnation-diffusion model was developed based on experimental data. The diffusion coefficient—a function of both temperature and pressure—increases with pressure at a power of 0.38 in the radial direction and 0.54 in the axial direction. The coefficient increases exponentially with temperature, following an Arrhenius-type correlation. Activation energy for radial and axial thermal diffusion was 2.8 and 3.2 kJ/g·mole, respectively, while the frequency factors were 2.7×10^{-7} and $113.3 \times 10^{-7} \text{ cm}^2/\text{s/K}^{1/2}$, respectively. The results indicate that impregnation of chemicals proceeds readily via axial diffusion and is not strongly dependent on temperature.

Application:

A model for predicting the time required to impregnate softwood chips prior to steam-explosion pulping.

summarize current knowledge about the transport of water and reactants within a softwood matrix (our prototype lignocellulosic material).

Softwoods are mostly wood fibers, or tracheids. These are hollow cellulosic tubes, tapered and closed at both ends, with rectangular and elliptical cross sections. Average fiber length is about 3.5–4.0 mm (2). Fiber diameter is 0.020–0.040 mm, but it can range from 0.015 mm to 0.080 mm (3–5). The fibers are laid down in fairly regular radial rows, with their long axes parallel to that of the tree. The tapered ends of the fibers overlap longitudinally by about one-fourth their length.

The fiber walls are made up almost entirely of cellulose and hemicellulose, which comprise about 70% of the dry weight of the wood (2). The fiber wall of the mature cell is composed of two layers: a thin outer layer (primary wall) and the thicker inner layer toward the cell cavity (secondary wall). The substance that cements the outer walls together is called the "intercellular layer or the middle lamella," which is mainly composed of lignin. In sections of wood tissue, the primary walls of two adjoining cells and the middle lamella, which cements these cells together, appear as one layer. This three-ply layer is called the "composed middle lamella" (6).

The hollow cavity at the fiber center is the lumen. Each fiber cavity has pits communicating with adjacent fiber cavities. There are two main types of pits: simple and bordered. All pits have two essential components: the pit cavity and the pit membrane. In the simple pit, the cavity is nearly constant in width, perhaps only gradually widening or narrowing toward the cell lumen. In the bordered pit, the cavity narrows more or less abruptly toward the cell lumen. Typically, the membrane is overarched by the secondary cell wall. The pit membrane consists of primary wall and middle lamella. As a rule, pits in the walls of adjoining cells appear in pairs (pit pairs), and the common membrane therefore is composed of two primary walls and middle lamella. The membrane pore dimension of a single layer of a moist primary wall of a softwood is on the order of 3.5–4.0 nm (7).

In living trees, moisture—defined as the water retained per unit weight of oven dry (o.d.) wood fiber—varies from about 30% to 300% (8, 9). This variation is influenced by different factors, such as tree species, position of wood section in the tree, and season of the year. In softwoods, heartwood has a moisture content of

30–65%, lower than sapwood, which has a moisture content of 100–200% (8, 10). In our experiments, moisture content varied across the collected green-wood tree log. The heartwood and sapwood regions had moisture contents of 27.9% and 135.4% (based on o. d. wood), respectively.

The moisture found in wood is in two forms: as liquid water in cell walls and as liquid and/or vapor in cell cavities. At saturated conditions, there is only liquid water (11). Stamm (12) has pointed out that natural green wood is never completely filled with water, so that practically all fiber cavities contain considerable air. The basic reason for moisture entering into the wood matrix is the hydrogen bonding of water molecules to the hydroxyl groups that are mainly present in the carbohydrate fraction. As a result, a monomolecular layer of water is readily formed. Under the effect of secondary attractive forces, more water molecules enter and can form a multimolecular layer. An additional amount of water can enter by capillary condensation in cell-wall voids and pit features (pit membrane openings, small pit mouths). After saturation of the walls, liquid water also can enter cell cavities (13, 14). The water held in cell walls is called "bound water," and the water held in cavities is "free water." The theoretical condition at which the walls are saturated but the cavities are empty is called the fiber saturation point (15). The fiber saturation point varies from species to species and even between heartwood and sapwood of the same wood log. Depending on the species, the average fiber saturation point of a tree log ranges between 20% and 35% (based on o. d. wood). The fiber saturation point decreases with the presence of resins (16).

Water (or other polar liquids in which wood swells) is adsorbed on the surface of the wood capillaries with a force considerably greater

than the mutual force of attraction between the molecules of the liquids themselves (17). The molecules of the swelling agents adsorbed on the surface must, consequently, be strongly attached. Hence the diameter of the molecules of the swelling liquid should be subtracted from the geometric radius to obtain the effective radius for passage. In the case of water, the cell-wall pore effective radius for passage is about 0.2 nm (12), which is much lower than the pore size of a single layer of a primary wall (3.5–4.0 nm). Through this fine cell-wall structure, small molecules can diffuse (2).

The impregnation of chemicals into wood chips has long been considered taking place via two processes: first, the mass flow through capillaries (lumens or cavities) of variable diameters; and second, diffusion from these capillaries through the cell wall and pit membrane structure. The force of capillary rise from the cut ends of chips initiates the impregnation, and continuity of the capillary flow toward the interior of the matrix (by capillary rise and subsequently by diffusion) is responsible for fluid penetration to the surface of the fiber walls in what appears to be a relatively rapid process (18). It has been reported that acid sulfite liquor penetrates into the longitudinal (or axial) wood structure 50–100 times faster than in the transverse (or radial in a cylindrical geometry) direction. This movement comes rapidly to a standstill as the liquid approaches the blind ends of the capillaries or as it approaches wood capillaries that are at the fiber saturation point or that contain liquid–air interfaces. Hydrostatic pressurization of the system reduces the size of the air bubbles somewhat and brings more wall surface in contact with the liquor, but the effect is small, since extremely high system pressures would be required to over-

come the resistance of the surface-tension forces of multiple liquid-air interfaces in the narrow capillaries (18). Beazley (19) has reported that this trapped air dissolves into the water to some extent, thus promoting diffusion. Maass and Lusby (20) have carried out impregnation of bulk spruce with water in the axial direction. They observed an increase of impregnation while increasing the temperature from 20°C to 50°C. This rise with temperature was explained as being due to three possible effects: (a) a decrease in the solubility of air in water, (b) more rapid diffusion of air molecules out of the chip, and (c) expansion of air in the chip, which assists in its removal. Apparently the last two are predominant. However, they could not describe the diffusion of water or solution into the wood chips with temperature via an Arrhenius-type correlation, which has been considered by other authors (21-23).

The term "transient" is used to designate capillaries that exist only when the membrane or cell wall is swollen (2). Stamm (24) has stated that in the case of pressure-induced flow (i.e., permeation), nothing goes through transient capillaries. These capillaries are so small that their effectiveness toward flow is negligible but, in the case of diffusion, it is not the size that counts but their number and the area. For this reason, in the case of diffusion, there may be quite an effective liquid diffusion through a transient capillary system. Even in a system where the major movement is vapor movement, when the vapor encounters an obstacle where there is no capillary big enough for vapor flow, the vapor condenses, and diffusion occurs as a liquid (i.e., surface diffusion) through the transient capillaries and then evaporates again on the other side.

Above the fiber saturation point, the larger capillaries contain free liquid. Water is held within the struc-

ture of wood membranes, pores, and capillaries in four different phases:

1. As water of constitution (by the formation of hydrates)
2. As surface-bound water or water in an adsorbed monomolecular layers with a high apparent density of 1.3 g/cm³
3. As water adsorbed in multimolecular layers with a decreasing order of dipoles approaching the density of 1.0 g/cm³ for liquid water
4. As capillary condensed water (25).

The molecules of water adjacent to the capillary walls are not free but bound by chemisorption. These sorbed molecules are, to a certain extent, parts of the capillary walls. There is evidence that with an increase in pH, the wood structure swells (26) because of increased accumulation of water molecules as bound water layer within the wood structure (27, 28), i.e., increasing the pH enhances the adsorption of water. This enhancement of water-layer adsorption also takes place on the capillary walls. Thus, the capillary pore diameters become much narrower, and the liquid movement then becomes difficult. Furthermore, each capillary pore is blinded by the pit membranes. The membranes are made of primary wall and middle lamella hosting a multimolecular layer of water molecules, leaving no void micropores. Any passage of chemical through these membranes is thus controlled by diffusion (7). Moreover, green wood always contains some trapped air. During pressure impregnation, the trapped air partially dissolves into solution and also can gradually diffuse out of the pores, while the liquid diffuses into the pores countercurrently. The overall transportation mechanism thus is controlled eventually by the movement through the hydrated mem-

brane pores, and it can be considered to be a diffusion mechanism.

MODEL DEVELOPMENT

Assumptions

All biomass materials are chemically heterogeneous because of the spatial structure of its three major constituents—cellulose, hemicellulose, and lignin—and because of the presence of crystalline and amorphous cellulose. Structural and physical properties thus will vary over the regions of a log cross section. To develop an impregnation model, we have made the following assumptions:

- Chemical impregnation is considered to follow diffusional laws that can be modeled based on Fick's second law of diffusion.
- Radial and tangential diffusion rates are not distinguished.
- During impregnation, NaOH concentration in the impregnating solution surrounding the wood sample remains constant.
- Both radial and axial diffusivities are independent of radial and axial position in the cylindrical samples.
- Heat-transfer limitations are considered negligible, i.e., the temperature is uniform through the sample.
- No chemical reactions occur between the matrix and the diffusing chemicals at the temperature of impregnation.

The diffusion coefficient of NaOH solution into wood is a pH (and thus concentration) dependent parameter (26). However, over a narrow range of concentrations, we will consider it to be independent (23). When NaOH solution concentration is above 4.25 wt.%, the diffusion constant remains unchanged (19). In the present model, diffusion is considered to be dependent only on pressure, temperature, and the nature of the biomass material.

Model

According to the absolute-reaction-rate theory, thermal effects on the diffusion constant can be represented as a function of absolute temperature, following an Arrhenius-type correlation (21, 29, 30).

$$D = A T^{1/2} e^{-E/RT} \quad (1)$$

where

- D = diffusion constant, cm^2/s
- A = pre-exponential constant in generalized equation, $\text{cm}^2/\text{s}/\text{K}^{1/2}$
- T = absolute temperature, K
- E = activation energy for diffusion, $\text{kJ}/\text{g}\cdot\text{mole}$
- R = ideal gas constant.

The absolute-reaction-rate theory can also be extended to cover the pressure influence on diffusion (31, 32), leading to Eq. 2.

$$D = D_0 T^{1/2} P^m e^{-E/RT} \quad (2)$$

where

- D_0 = frequency factor, $\text{cm}^2/\text{s}/\text{K}^{1/2}$
- P = dimensionless pressure term, i.e., the ratio of absolute pressure to atmospheric pressure
- m = pressure power factor.

During the impregnation of chemicals in wood, the sample becomes swollen to different degrees. Diffusion into or from the substrate is more complicated than through a rigid material. However, for a given agent concentration in solution (NaOH in the present case), the swollen matrix will be considered as having an invariant geometry with time. Under these conditions, we can express the diffusion process by Fick's second law of diffusion (33). Its differential form in cylindrical coordinates is expressed by Eq. 3 (34, 35):

$$\partial C/\partial t = \{[(1/r) (\partial/\partial r) r D_r (\partial C/\partial r)] + [(\partial/\partial z) D_z (\partial C/\partial z)]\} - k C^\phi \quad (3)$$

where

- C = concentration of the diffusing chemical at a local position (r, z), g/cm^3
- t = time, min
- r = radial penetration, mm
- z = axial penetration, mm
- D_r = radial diffusion constant, cm^2/s
- D_z = axial diffusion constant, cm^2/s
- k = rate constant for reaction between chemical and matrix
- ϕ = reaction order.

If we assume that there is no chemical reaction—or that any chemical reaction that occurs is kinetically irrelevant—and that the diffusion constants are independent of position, then Eq. 3 can be simplified as follows:

$$\partial C/\partial t = \{D_r (1/r) (\partial/\partial r) [r(\partial C/\partial r)]\} + [D_z (\partial^2 C/\partial z^2)] \quad (4)$$

From a given impregnation experiment, Eq. 4 needs to be solved to obtain the radial and axial diffusion constants. An optimization method will be used to test the experimental data. Our approach is to test the model separately in two different directions (radial and axial) so that we can verify the validity of the diffusional mechanism in each direction. Therefore, we have isolated the radial directional impregnation from the axial one (and vice versa) by sealing the outer surface in the radial or axial directions using a thin layer of sealing materials with thermal properties similar to those of wood. Equation 4 is thus uncoupled into two separate equations representing two different directions: radial concentration equation only and axial concentration equation only. This agrees with our stated assumption that there is no interplay

between radial and axial transport processes.

Equations for radial concentration profile.

$$\partial C/\partial t = D_r (1/r) (\partial/\partial r) [r(\partial C/\partial r)] \quad (5)$$

The initial and boundary conditions (IC and BC, respectively) are given in Eqs. 6–8.

$$\text{IC: } C = 0 \text{ at } 0 \leq r \leq a \text{ at } t = 0 \quad (6)$$

$$\text{BC: } C = C_0 \text{ at } r = a \text{ at } t \geq 0 \quad (7)$$

$$\text{BC: } C = \text{finite at } r = 0 \text{ at } t \geq 0 \quad (8)$$

where

- C_0 = chemical concentration at the edge of the sample
- a = radius of the cylindrical sample, mm.

The analytical solution of Eq. 5 satisfying the initial and boundary conditions set in Eqs. 6–8 is given in Eq. 9 (34, 35).

$$C/C_0 = 1 - (2/a) \sum_{n=1}^{\infty} \{ [J_0(r\alpha_n)] / [\alpha_n J_1(\alpha_n)] e^{-D_r \alpha_n^2 t} \} \quad (9)$$

where

- J = Bessel function
- n = series number in Bessel function (1, 2, 3, ..., n)
- α_n = roots of $J_0(\alpha_n) = 0$ (dimensionless)
- D_r = radial diffusion constant, cm^2/s
 $= D_{0,r} T^{1/2} P^m e^{-E_r/RT}$.

Equation 9, simplified by substituting the dimensionless quantity $\beta_n = a\alpha_n$, yields Eq. 10.

$$C/C_0 = 1 - 2 \sum_{n=1}^{\infty} \{ [J_0(r\beta_n/a)] / [\beta_n J_1(\beta_n)] e^{-\beta_n^2 D_r t/a^2} \} \quad (10)$$

where

$\beta_n =$ roots of $J_0(\beta_n) = 0$ (dimensionless).

Equations for axial concentration profile.

$$\partial C/\partial t = D_z(\partial^2 C/\partial z^2) \quad (11)$$

The initial and boundary conditions are given in Eqs. 12–14.

$$\text{IC: } C = 0 \text{ at } z > 0 \text{ at } t = 0 \quad (12)$$

$$\text{BC: } C = C_0 \text{ at } z = 0 \text{ at } t > 0 \quad (13)$$

$$\text{BC: } C = C_0 \text{ at } z = \infty \text{ at } t > 0 \quad (14)$$

The analytical solution of Eq. 11 satisfying the initial and boundary conditions set in Eqs. 12–14 is given in Eq. 15 (34):

$$C/C_0 = 1 - \text{erf}\{z/[2(D_z t)^{1/2}]\} \quad (15)$$

where

erf = error function

$$D_z = \text{axial diffusion constant, cm}^2/\text{s} \\ = D_{0,z} T^{1/2} P_z^m e^{-E/RT_z}$$

If we consider Na as the diffusing chemical, we can measure the local X-ray intensity, which is proportional to the concentration (36). Therefore,

$$C_{\text{Na}} = \kappa I_{\text{Na}}$$

$$C_{0,\text{Na}} = \kappa I_{0,\text{Na}}$$

where

κ = proportionality constant

I = Na-element X-ray intensity as measured locally (by slicing the sample)

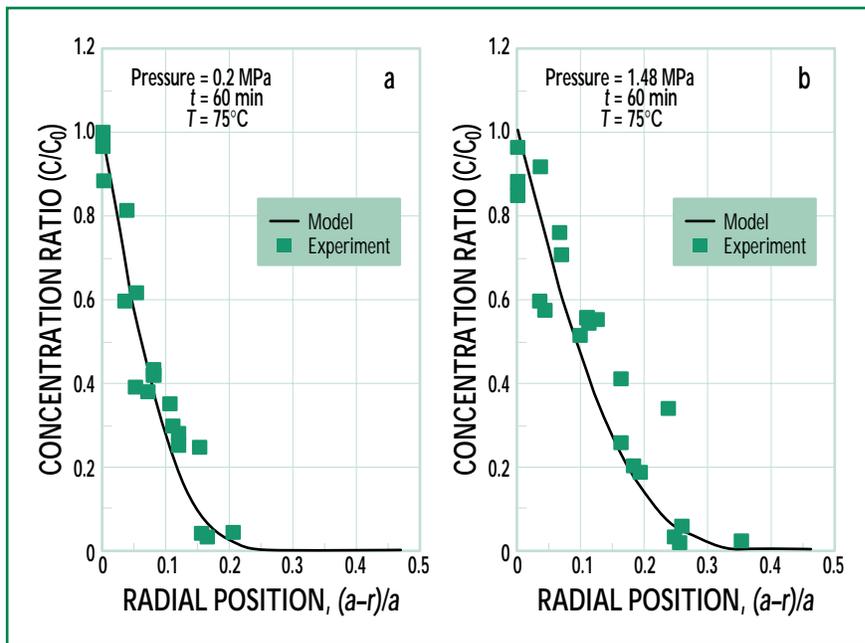
I_0 = Na-element X-ray intensity as measured at the sample edge.

From the previous equations, it follows that the ratio C/C_0 will be the same as I/I_0 . Therefore, Eqs. 10 and 15 can be solved using I/I_0 rather than C/C_0 .

Diffusion direction	Frequency factor (D_0), $10^{-7} \text{ cm}^2/\text{s/K}^{1/2}$	Pressure power factor (m)	Activation energy (E), kJ/g-mole	E/R , K
Radial ^b	2.70	0.38	2.8	338.7
Axial	113.3	0.54	3.2	384.0

^a Values were determined from experiments using 14 samples impregnated at different pressures, temperatures, and times with a 10 wt.% NaOH aqueous solution.
^b Radial diffusion relates to both radial and tangential directions.

1. Diffusion parameters for impregnation of softwood^a

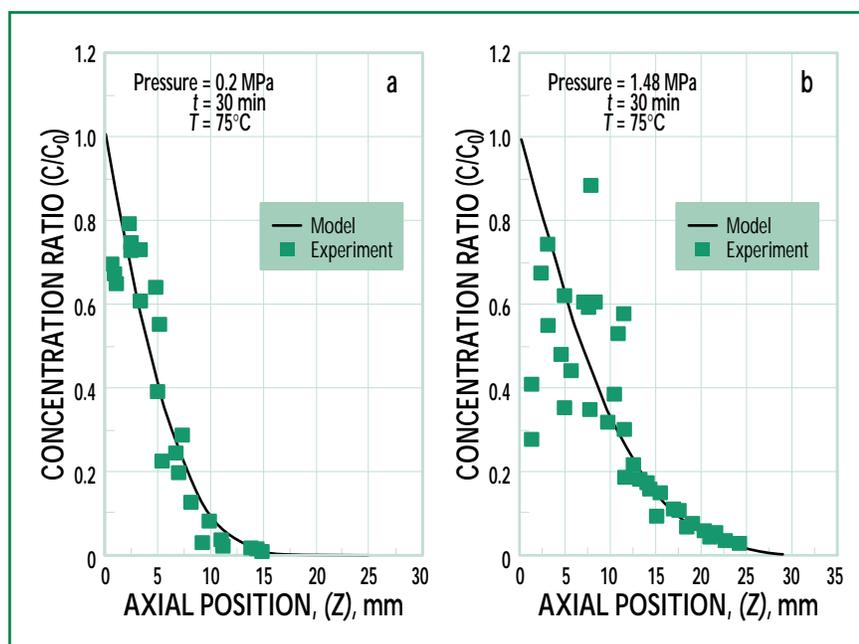


1. Radial concentration profiles following softwood impregnation with NaOH solution (10 wt.%) at (a) 0.2 MPa and (b) 1.48 MPa (75°C, 60 min; sample size: length, $Z = 150$ mm; radius, $a = 15$ mm)

EXPERIMENTAL

Black spruce of about 40 years of age was collected from the Eastern Townships, PQ. A representative log was split into two sections: the outer portion (edge) and the inner, central portion. The central region represents the heartwood section, whereas the edge represents sapwood. Physical properties within each section were assumed constant. Since heartwood is more difficult to impregnate than sapwood (37), the heartwood section was chosen for study. The softwood sample had an average moisture content of 27.9% (water retained per weight unit of o.d. wood). To preserve the moisture content, all samples were stored in polyethylene bags at -4°C .

To study the chemical impregnation, a cylindrical prototype sample (radius $a = 15$ mm, length $Z = 150$ mm) was prepared using a lathe. The axis of the prototype sample is parallel to the fiber axis, and the radial surface represents the radial and tangential surfaces of the softwood. To isolate the axial-diffusion impregnation process from the radial-diffusion process, the sample's axial surfaces were well sealed by a thin layer of epoxy and a rubber gasket. The radial surface was kept bare to let NaOH diffuse. Similarly, for axial impregnation, the radial surface was sealed, and the axial surfaces (top and bottom of the cylindrical sample) were left bare.



2. Axial concentration profiles following softwood impregnation with NaOH solution (10 wt.%) at (a) 0.2 MPa and (b) 1.48 MPa (75°C, 30 min; sample size: length, $Z = 150$ mm; radius, $a = 15$ mm)

The bare surfaces were exposed to a solution of 10 wt.% NaOH in the impregnator for 60 min and 30 min for radial and axial impregnation, respectively, at a constant temperature of 75°C and at four different pressures of 0.2, 0.79, 1.48, and 2.17 MPa. A similar set of experiments was done at a fixed pressure of 1.48 MPa for three different impregnation temperatures of 25°C, 50°C, and 100°C. The impregnator was an annular cylindrical vessel fitted with a pneumatic piston. Hot water was circulated through the annular space to ensure a uniform temperature. The pneumatic piston was used to control the impregnation pressure. After completion of the impregnation, the samples were kept in a refrigerator at freezing temperature to prevent further diffusion.

The frozen sample was sliced using a fine power saw. Sliced samples were dried in a freeze dryer to avoid any secondary thermal diffusion. These dried samples were then polished by different grades of sandpaper to make a smooth surface for SEM (scanning electron microscopy) analysis. Finally, samples were coated

with Au-Pd coating, and liquid silver was used to make the sample electrically conductive as a prerequisite for SEM analysis.

It is likely that some ice crystals formed in the initial sample during storage in the freezer, prior to impregnation. To avoid the possibility of ice crystals blocking chemical impregnation, all samples were removed from the freezer about two days before impregnation and kept at room temperature in a polyethylene bag for total defrosting while keeping its moisture intact. In order to analyze the sample by SEM, the samples were freeze-dried after impregnation to avoid any type of secondary thermal diffusion.

The impregnation of the 10-wt.% NaOH solution into wood was traced by taking the Na-element as marker. Impregnation of NaOH solution induces a yellowish color in contact with the softwood, which helps in locating the extent of NaOH impregnation visually. The darkness of the color and the extent of impregnation depends on the severity of treatment.

The 10-wt.% NaOH makes a layer on the base surface with essentially the same concentration as that of the bulk solution. After stopping the impregnation, this thin layer stays on the surface at the edge of the sample. This layer eventually makes the boundary condition to be the same for each sample. In order to estimate Na-element distribution via X-ray intensity measurement, most of the points near to the edge were chosen within the colored zone. One or two points were also taken outside the colored zone.

X-ray intensity was measured at different points over the colored region, including one point near the sample edge, and also at one or two locations beyond the colored region by SEM (JEOL: model no. JSM-840A). During X-ray analysis, a voltage of 15 kV, a probe current of 9×10^{-9} amp, and a working distance of 39 mm were used. From the X-ray intensity data, the intensity at the edge of the sample was obtained by extrapolation, and this was set as I_0 . The ratio of intensity I , measured at different radial positions to I_0 , was calculated for each experiment. Since the ratio I/I_0 is the same as that of concentration, C/C_0 , I/I_0 values were used in Eqs. 10 and 15. To obtain the diffusion parameters, D_0 , m , and E/R , the concentration equations were solved via the FMINS program of the MATLAB package (38) using 150 roots of Bessel's functions (39).

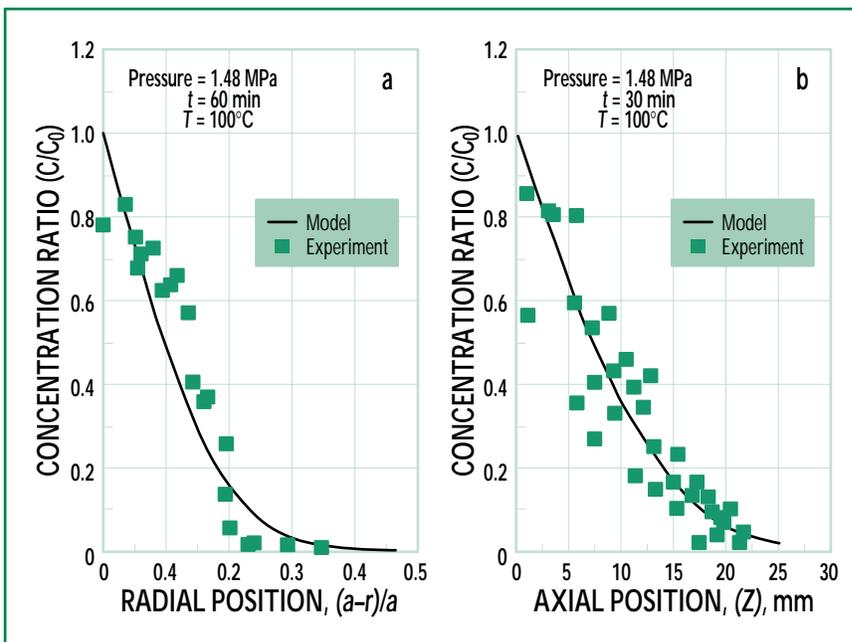
RESULTS AND DISCUSSION

For the SEM analysis, the samples were sliced and polished manually with different grades of sandpaper. Consequently, the contact between hand gloves and sample edge may have caused some loss of Na-element from the sample edge, leading to a lower Na-element X-ray intensity at the edge than that obtained from the points just away from the edge. Intensity count, which is proportional to Na-element concentration, depends

on many factors, including the probe current, voltage, vacuum pressure, working distance, and instrument stability. However, for each analysis, all these factors were kept unchanged. Since all of the samples were not examined in the same day, a slight variation of these factors among the samples is likely to occur, causing a variation of the intensity count. However, the ratios of these intensities are essentially the same. Thus, whenever the intensity ratio (I/I_0) is calculated, it gives a result independent of the small variations in the SEM conditions for each experiment.

Since the concentration ratio, C/C_0 , is equal to intensity ratio, I/I_0 , these values were used in Eqs. 10 and 15 to calculate the radial- and axial-diffusion constant parameters, D_r , m , and E for each impregnated sample. From the multiple experiments conducted with different samples (a total of 14 samples was used in our work), average diffusion constant parameters were determined for (a) the radial diffusion that relates to the radial and tangential directions of the wood fiber and (b) the axial diffusion that relates to the axial direction of the fiber. The results are shown in **Table I**. The average values for these parameters were used in the radial- and axial-impregnation model equations to obtain the concentration profiles.

The concentration profiles obtained from the model and from experimental results are shown for both radial and axial impregnations (at a constant temperature of 75°C for two pressures, 0.2 and 1.48 MPa) in **Figs. 1 and 2**, respectively. **Figure 3** shows the radial and axial profiles at a pressure of 1.48 MPa and temperature of 100°C. From Figs. 1-3 we can infer that impregnation proceeds as two “diffusion fronts”—radial and axial—and that the time constants of these two diffusion fronts are quite different, as clearly identified by the parameters in **Table I**.



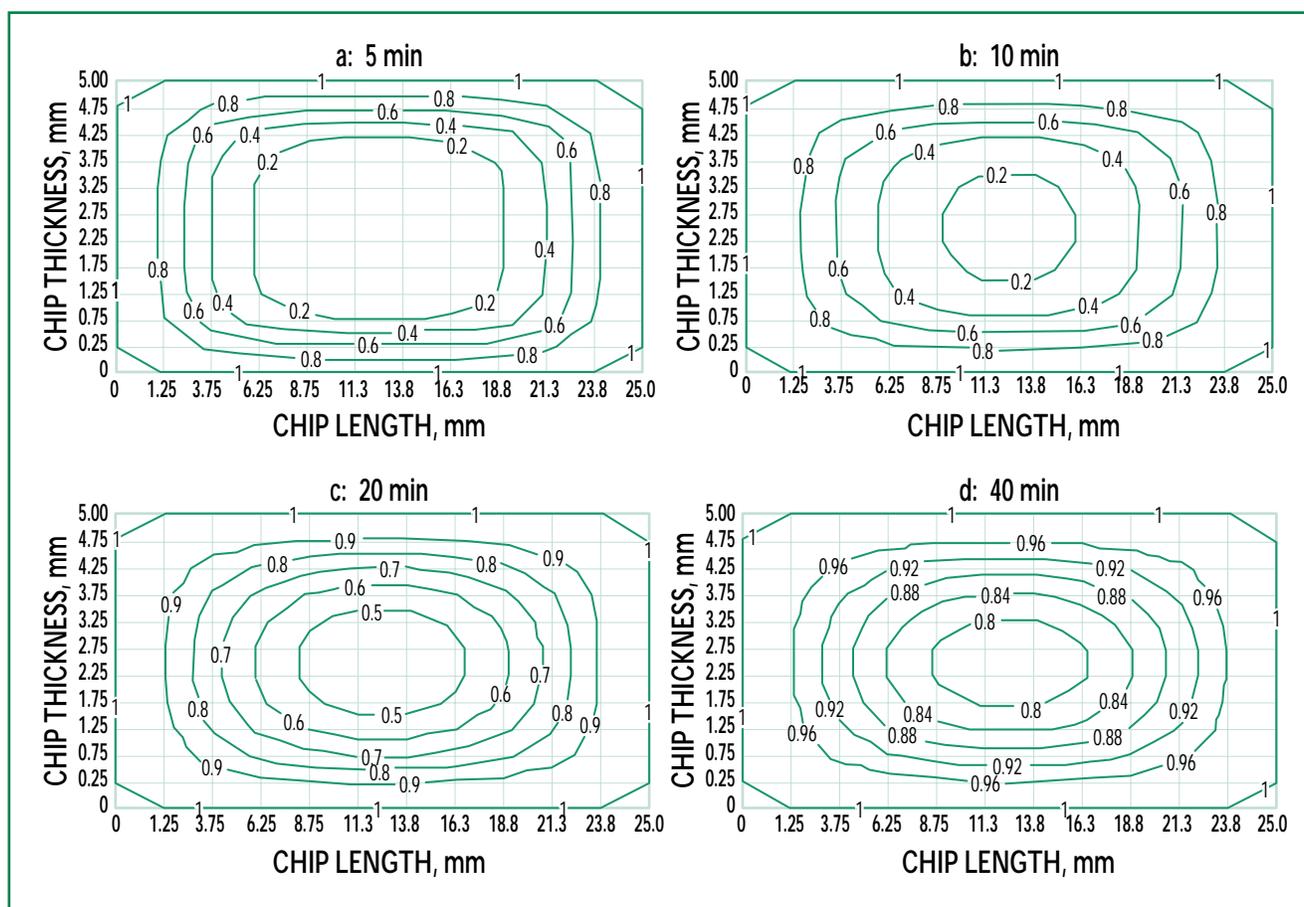
3. (a) Radial and (b) axial concentration profiles following softwood impregnation with NaOH solution (10 wt.%) at the specified conditions (sample size: length, $Z = 150$ mm; radius, $a = 15$ mm)

The experimental results are somewhat scattered. This is due to the roughness on the sample surfaces obtained after grinding the samples with different grades of sandpaper. During grinding, the edges of the samples were most vulnerable to the sand particles, causing a higher roughness than at any other places on the surface, resulting in higher scatter. However, the experimental and the model results showed good agreement in all cases, indicating that the assumptions made in model development were reasonable.

The objective of developing the impregnation model was to obtain the required time to reach a steady-state concentration distribution within the chips for a rapid pulping process. These chips are small and rectangular in shape, with dimensions of about 5 mm in thickness, 15–25 mm in width, and 10–30 mm in length. The diffusion values in the direction of thickness and width are the same and equal to the radial value of our cylindrical prototype sample. The radial- and axial-impregnation model parameters obtained

from our experimental results were used in the overall impregnation model, Eq. 4, which was solved by SIMPLER (40) to find (a) the progression of the impregnation front as a function of time, as shown in **Fig. 4**, and (b) the overall impregnation time needed to reach a 99% steady-state concentration at the center of chips of various length for a range of impregnation conditions, as shown in **Fig. 5**. From **Fig. 5**, it is clear that the required impregnation time is reduced with increasing pressure and temperature. Since the hemicellulose begins to degrade at or below 100°C for the prolonged treatments (41), we used an impregnation temperature of 75°C to ensure no degradation. From the simulation results in **Fig. 5**, we can conclude that there is no significant influence of pressure beyond about 2.17 MPa. At this pressure, our simulation results show that at 75°C, an impregnation time of 75 min is required to reach 99% of the steady-state concentration at the center of a softwood chip 5 mm in thickness and 20 mm in length.

Since the diffusion coefficient depends on temperature (following



4. Simulated results showing concentration (C/C_0) profiles of a softwood chip (thickness 5 mm; length 25 mm) at different impregnation times. Simulation represents impregnation with NaOH solution (10 wt.%) at a pressure of 2.17 MPa and a temperature of 75°C for (a) 5 min, (b) 10 min, (c) 20 min, and (d) 40 min.

an Arrhenius-type correlation), the activation energy can be obtained using a graphical method simply by plotting Eq. 2 as $\log(D/T^{1/2})$ against $1/T$. This gives a straight line with a slope of $-E/R = 327.89$, as seen in Fig. 6, whereas from the numerical optimization technique, the value obtained was 338.7. Since the activation-energy term calculated by the numerical method was averaged over the entire population of results, the numerically obtained results are considered more representative.

From the numerical optimization method, the activation energies for thermal diffusion in the radial and axial directions were found to be 2.8 and 3.2 kJ/g-mole, respectively, suggesting that the diffusion requires little activation. Gustafson *et al.* (22) obtained an activation energy of 20.4 kJ/mole in their simulation studies. Similar values were also obtained by Talton (21) and Lönnberg *et al.* (23). Why do our results differ? There are several explanations:

1. The activation energy for NaOH diffusion into wood chips depends largely on the experimental method used and on the method of data analysis. Talton (21) and Lönnberg *et al.* (23) used Fick's first law of diffusion applied to a steady-state situation where diffusion occurs from the

impregnated wood chips to the water solution surrounding the chips. In this situation, fluxes and surface areas of the chips are used. Since the surfaces of wood chips are normally rough, the effective surface area is much higher than the geometric area. Accounting for this effect would eventually lead to lower activation energies. In our case, the diffusion constant was calculated by using Fick's second law of diffusion (applied to an unsteady-state situation), where we need not use the surface area.

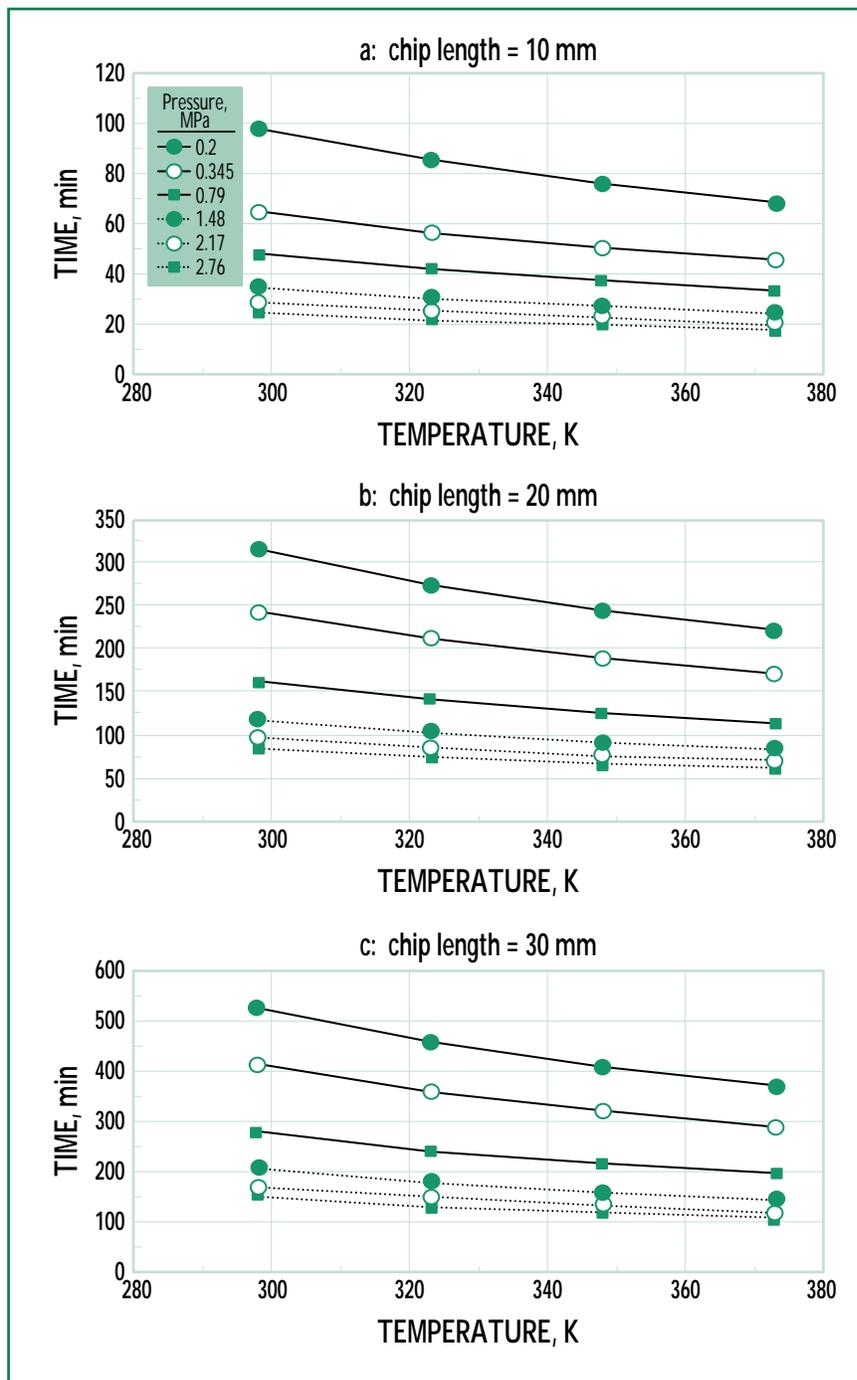
2. During impregnation, the diffusing NaOH solution comes in contact with the wood components, leading to adsorption of NaOH onto the wood matrix. Adsorption is an exothermic process and thus releases energy (42). Most

KEYWORDS

Activation, bibliographies, diffusion, impregnation, lignocellulose, models, softwood pulping.

researchers (21, 30) have obtained the diffusion coefficient by measuring the concentration change in a water bath where a wood block previously impregnated with NaOH solution is submerged. The release of NaOH from the wood block takes place by two mechanisms: desorption followed by diffusion out of the chips. Therefore, the activation energy obtained from these studies very well may be related to the desorption step which, as the reverse of the adsorption, needs to be activated.

The influence of pressure on pulping has long been observed (43-45), but the mechanism to describe this influence in the impregnation of wood chips with chemicals has not been considered in depth. Some researchers (46-48) have considered that the pressure influences the capillary flow of the chemicals through the capillary pores of the wood chips. This concept could be true for small chips, i.e., the chips that have a length lower than the length of a fiber cell (or tracheid). In this case, the chips consist of double-cut cells without any bordered pits. However, the concept of capillary flow is not applicable to green-wood chips larger than the cell length. Green-wood chips are saturated with water above the fiber saturation point, which means that the pore dimensions of pits, membranes, and cell-wall pores are being changed to dimensions through which the chemicals can only be transported by diffusion mechanisms (7). The applied impregnation pressure may change somewhat the dimensions of the cavities of the wood samples by compressing them, and it also may affect the diffusion coefficient for chemical diffusion into wood chips (29). In the present case, the diffusion coefficient has been considered to be proportional



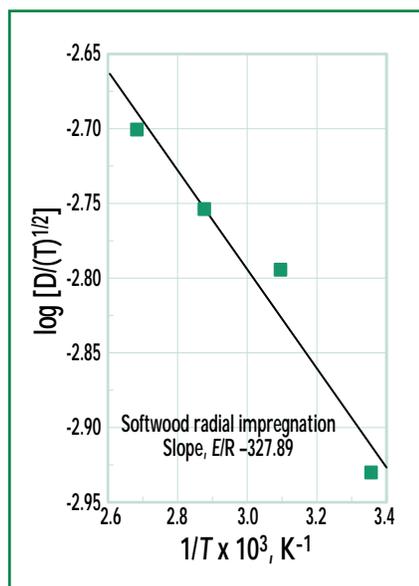
5. Simulated results showing the time required to achieve impregnation concentration (C/C_0) of 99% at the center of a 5-mm-thick softwood chip in NaOH solution (10 wt.%) for chips of length (a) 10 mm, (b) 20 mm, and (c) 30 mm

to the dimensionless pressure with a power factor of m . The pressure power factors for radial and axial direction of softwood were found to be 0.38 and 0.54 (Table D), respectively. The pressure power factor in the radial direction is less than that for the axial direction, which means

that the influence of pressure is magnified in the axial direction.

CONCLUSIONS

Chemical impregnation into softwood chips having a moisture content above the fiber saturation point can be modeled by diffusion mecha-



6. Plot of $\log[D/(T)^{1/2}]$ vs. $1/T$ to obtain the slope as an estimator of E/R

nisms. Wood anisotropy can be taken into account by considering only radial and axial mechanisms.

The activation energies for thermal diffusion in the radial and the axial directions are 2.8 and 3.2 kJ/g-mole, and the pressure power factors are 0.38 and 0.54, respectively.

Simulation results indicate that at an impregnation pressure of 2.17 MPa and a temperature of 75°C, the required impregnation time for a Na concentration equal to 99% of the concentration at the outer surface (10 wt.% NaOH in solution) can be achieved in 75 min for chips having a length of 25 mm and a thickness of 5 mm.

The proposed model is a valuable tool for predicting the pre-impregnation time needed to achieve a given concentration of a prototype chemically active agent (Na). The consequences for rapid steam treatment at high temperatures and short times are obvious.

Rapid steam pulping (2–4 min) can be achieved only with prior impregnation that will ensure uniform distribution of the active chemicals. To our knowledge, the significance of pre-impregnation has been overlooked in all previously published work on “steam-explosion” treatments applied to pulping and to hydrolysis in general. **TJ**

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NOMENCLATURE

a = radius (thickness) of the cylindrical prototype sample, mm	D_z = axial diffusion constant, cm^2/s	r = penetration in radial direction, mm
A = pre-exponential constant in a generalized equation, $\text{cm}^2/\text{s}/\text{K}^{1/2}$	E = activation energy, kJ/g-mole	R = ideal gas constant
C = chemical concentration, g/cm^3	I = X-ray intensity (arbitrary constant)	t = time, min
C_0 = concentration at the edge (outer surface) of the sample	I_0 = X-ray intensity at the sample edge (arbitrary constant)	T = absolute temperature, K
D = diffusion constant, cm^2/s	J = Bessel's function	z = penetration in axial direction, mm
D_0 = frequency factor, $\text{cm}^2/\text{s}/\text{K}^{1/2}$	k = reaction rate constant	Z = length of the prototype cylindrical sample, mm
D_r = radial diffusion constant, cm^2/s	m = pressure power factor	α_n = roots of $J_0(a) = 0$
	n = series number (Bessel's function)	β_n = dimensionless quantity
	P = dimensionless pressure term	κ = proportionality constant
		ϕ = reaction order
		∞ = infinite