

Modeling resin extraction from wood with different solvents

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ABSTRACT *A model for resin extraction from wood is proposed. This model assumes three types of resin: in the pore mouth (easily accessible), inside the wood pores, and a third type contained in the epithelial cells, around the pores, inside the resin ducts. The dissolution rate for each resin type is described using macroscopic equations, and the rate coefficients of free solubilization are calculated for the four solvents studied: propanone, ethanol, trichloromethane, and diethylether. Other model parameters, such as mass transfer coefficients and saturation resin concentration are calculated by nonlinear regression to experimental data collected on a pilot plant scale, assuming that resin extract is 50% of the total wood extracts. The fit of experimental data is excellent. One conclusion is that ethanol is not able to dissolve resin inside the epithelial cells.*

KEYWORDS

Equations
Extraction
Mass transfer
Models
Pilot plants
Resin
Saturation
Solvents
Wood

In a previous paper (1), it was shown that wood extraction with solvents is a suitable operation for the recovery of some minor compounds, such as fatty and resin acids, and turpentine. Moreover, the extracted wood chips can be used for pulp and paper production; in that way, pulp obtained by the NSSC process from previously extracted *Pinus pinaster* wood can be a substitute for unbleached bisulfite wood.

In another work (2) the kinetics of wood extraction was established for solvents with strong extraction power, such as propanone, trichloromethane, and diethylether, and for solvents of weak extraction power—such as ethanol or benzene derivatives. It has been proposed (2) that wood extraction takes place along three steps: first, solubilization of the resin in easily accessible places, followed by solubilization of the solute inside the wood pores, and finally solubilization of relatively inaccessible solute, such

as the resin inside the epithelial cells.

In this work, a phenomenological model is proposed for the resin solubilization process, based on three steps:

- Solubilization of the resin in the pore mouth, easily accessible to the solvent.
- Once the resin in the mouth of the pores has fully dissolved, solubilization of the resin filling the wood pores begins.
- The third step, solubilization of the resin inside the epithelial cells, starts when, due to the solubilization of the resin in the pores, these cells become accessible to the solvent.

Transport and kinetic coefficients for each of these phenomena are calculated, and a final comparison is made between predicted and experimental results.

Experimental

A pilot plant extractor of 20 L was used. This extractor consisted of a stainless steel vessel fitted with an 11-L basket able to hold up to 3 kg of chips immersed in the solvent.

The experiments were carried out in batches. The extractor was heated by a closed circuit jacket to the boiling temperature of the solvent, at a constant solvent flow. The total extraction time was 9 h, with 60 min heating.

The extract solution was continuously collected in a 50-L evaporator and was partially recirculated to the extractor. Temperature, flow rate, and pressure were measured and controlled at the levels previously fixed.

Samples were collected from the evaporator through a valve every 30–60 min. The results are expressed as concentration of solid extracted, in units of grams of extract per liter of extract solution.

I. Experimental results

Time, h	Propanone Ex, g	Ethanol Ex, g	Trichloro- methane Ex, g	Diethylether Ex, g
0.50	3.49	1.51	3.37	3.36
0.75	8.02	2.83	8.08	6.80
1.00	12.85	4.24	13.33	10.70
1.25	17.09	5.64	18.12	14.70
1.50	20.41	6.96	22.00	18.58
1.75	22.81	8.17	24.90	22.18
2.00	24.46	9.25	26.95	25.45
3.00	28.71	12.96	32.17	34.89
4.00	31.75	16.15	35.67	40.50
5.00	34.16	19.01	38.31	44.45
6.00	36.18	21.64	40.43	47.40
7.00	37.93	24.08	42.70	49.72
8.00	39.48	26.37	43.71	51.60
9.00	40.88	28.55	45.03	53.16

II. Wood geometry

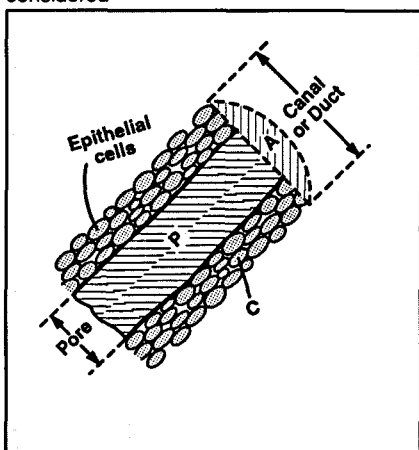
Chips: length: 3.00 cm
surface: 32 cm²/g
ducts: 2 ducts/cm²

Ducts: diameter: 2.45×10^{-2} cm
cross section: 4.714×10^{-4} cm²

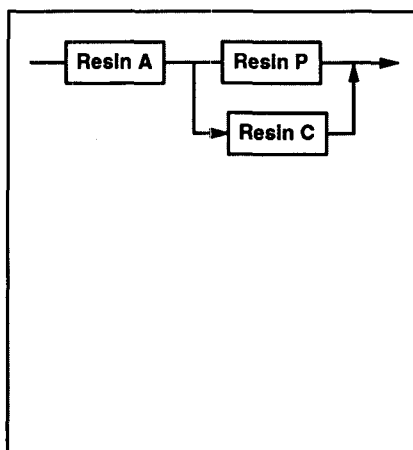
Pores: diameter: 1.75×10^{-2} cm
cross section: 2.405×10^{-4} cm²
distribution: 85% of 0.2 cm in length
15% of 1.5 cm in length
average length = 0.395 cm

Epithelial cells: depth: 3.50×10^{-3} cm

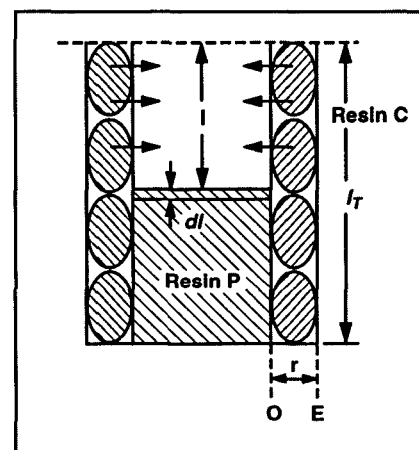
1. Diagram of a resin duct and types of resin considered



2. Scheme of resin solubilization



3. Diagram of a pore



Materials used

The wood chips were *P. pinaster*, with an average size of 21 mm, with a distribution size given elsewhere (1). The chips were conditioned at 20°C and 60% RH.

The solvents used were diethylether, propanone, ethanol, and trichloromethane, which have an extracted level (according to TAPPI Test Method T 204) of 2.73, 2.61, 2.60, and 2.75% oven-dry weight, respectively (1).

Experimental results

The analysis of samples collected from the evaporator at different times yielded the results given in Table I for the different solvents used. As shown previously (1), ethanol always extracted the least amount of total

resin. After 9 h of extraction, the total resin extracted by diethylether and trichloromethane was approximately the same, and greater than that extracted by propanone (1). The extraction rate increased throughout the first hour and later progressively decreased for all solvents. This is in accordance with the results reported by other authors (3-5).

Model for wood extraction

To develop a model for wood extraction, some idealization is required because of the complex internal structure of the wood. It can be assumed that resin extraction takes place mainly inside the resin ducts of the wood, because resin is found mainly in these

ducts and it is also the main extract component, as it constitutes half of the total extracted amount. If a resin duct is described as shown in Fig. 1, then the total resin can be considered to be divided into three types:

- Resin A, easily accessible at the opening of the duct. This resin is segregated by the epithelial cells when the wood is cut.
- Resin P, inside the resin pore. This resin is accessible to the solvent once Resin A has been fully dissolved.
- Resin C, inside the epithelial cells, on the walls of the resin ducts. This resin becomes accessible to the solvent by cell wall breaking or by osmosis or by both through the cell wall as Resin P is dissolved.

III. K and t_A values

Solvent	$K \times 10^4$, g/cm ² ·s	t_A , s
Propanone	16.36	5.4
Ethanol	3.43	25.6
Trichloromethane	10.82	8.1
Diethylether	20.37	4.3

IV. K' and K'' values

Solvent	$K' \times 10^4$			$K'' \times 10^8$		
	Opt.	Min.	Max.	Opt.	Min.	Max.
Propanone	0.500	0.458	0.542	6.929	5.891	7.967
Ethanol	0.161	0.150	0.171	-0.226	-1.14	0.689
Trichloromethane	0.525	0.487	0.562	9.995	9.023	10.972
Diethylether	0.435	0.399	0.471	15.094	14.11	16.082

In this manner, the solubilization of the resin can be described according to the scheme given in Fig. 2, in which the solubilization of Resin A is a necessary first step and then, in parallel, Resins P and C are dissolved.

Mathematical modeling

Assuming that Resin A presents to the solvent a surface S_A , constant with time, the solubilization rate can be described by Eq. 1:

$$-dm_A / S_A \cdot dt = K \quad (1)$$

where K (g/cm²·s) is the free solubilization rate, a parameter for each solvent. Integrating Eq. 1, taking into account a boundary condition such as Eq. 2, Eq. 3 is obtained:

$$t = 0, m_A = m_{A0} \quad (2)$$

$$m_{A0} - m_A = K \cdot S_A \cdot t \quad (3)$$

There will be a time, t_A , when all of Resin A will have been dissolved, and m_A will be zero, as given by Eq. 4.

$$t_A = m_{A0} / K \cdot S_A \quad (4)$$

At that moment, Resin P is accessible to the solvent, and the solubilization of this type of resin begins. Almost at the same time, when the solvent starts to dissolve Resin P, the solvent also begins to solubilize Resin C in the pore wall, and the epithelial cells are supplying more resin from inside those cells. At a given time, when the front of non-solubilized Resin P is located at a position l inside the pore (Fig. 3),

a mass balance in a differential volume inside the pore yields Eq. 5:

$$D \cdot (\partial^2 C_P / \partial l^2) = (\partial C_P / \partial t) + R_C \quad (5)$$

with the boundary conditions given by Eqs. 6A to 6C

$$t = t_A, C_P = C_{P0} \quad (6A)$$

$$l = 0, D \cdot (dC_P / dl) = K_L \cdot (C_P - C_R) \quad (6B)$$

$$l = l_T, C_P = 0 \quad (6C)$$

where R_C is the rate at which pore-wall cells are providing Resin of type C because some of the cells are accessible to the solvent.

Due to the difficulty of knowing the diffusion coefficient, D , a more simple maximum gradient model can be established, according to the following assumptions:

Total amount of Resin P can be calculated from Eq. 7:

$$m_{P0} = l_T \cdot S_P \cdot \rho \quad (7)$$

Therefore, at a time t :

$$m_P = (l_T - l) \cdot S_P \cdot \rho \quad (8)$$

Assuming that S_P is constant, from Eqs. 7 and 8 it can be deduced that the amount of Resin P dissolved is given by Eq. 9:

$$m_{P0} - m_P = l \cdot S_P \cdot \rho \quad (9)$$

Therefore, the dissolution rate is given by Eq. 10:

$$\rho (dl/dt) = K'_L (C_R^e - C_P) \cong K' \quad (10)$$

Due to the great difference between saturation concentration, C_R^e , and Resin P concentration, C_P , this rate can be assumed to be approximately constant, and therefore after integration of Eq. 10, with the boundary condition expressed by Eq. 11, Eq. 12 is obtained:

$$t = t_A, m_P = m_{P0} \quad (11)$$

$$m_{P0} - m_P = K' \cdot S_P \cdot (t - t_A) \quad (12)$$

There is a time, t_P , at which Resin P is fully dissolved:

$$t_P = (m_{P0} / K' \cdot S_P) + t_A \quad (13)$$

Resin C starts to dissolve, in parallel with Resin P, once Resin A has disappeared. This process can be described by Eq. 14:

$$D' \cdot (\partial^2 C_C / \partial r^2) = \partial C_C / \partial t \quad (14)$$

With boundary conditions given by Eqs. 15A to 15C:

$$t = t_A, C_C = C_{C0} \quad (15A)$$

$$r = 0, D' \cdot (dC_C / dr) = R_C \cdot f \quad (15B)$$

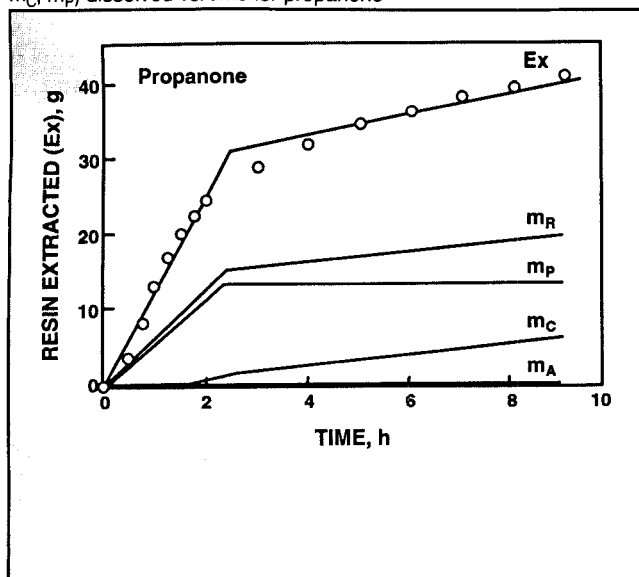
$$r = E, D' \cdot (dC_C / dr) = 0 \quad (15C)$$

Because of the same difficulty stated for the description of Resin P, a maximum gradient model can be applied, describing the dissolution rate by Eq. 16:

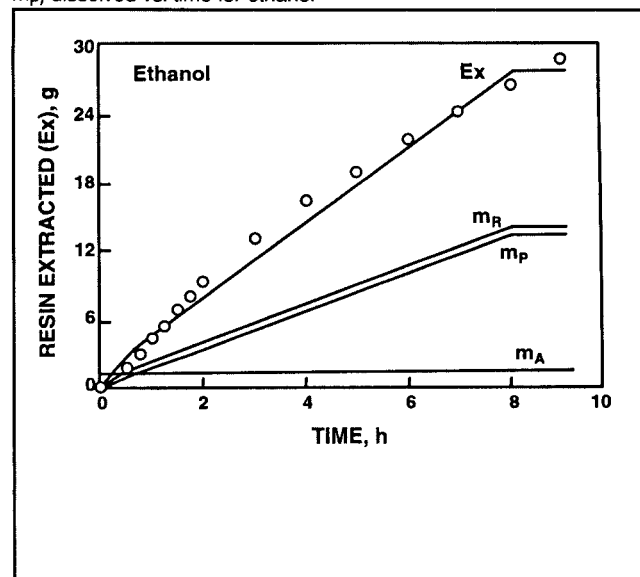
$$- (dm_C / S_C \cdot dt) = K''_L \cdot (C_R^e - C_C) \cong K'' \quad (16)$$

Taking into account the boundary

4. Extractives (Ex), total resin (m_R), and different types of resin (m_A , m_C , m_P) dissolved vs. time for propanone



5. Extract (Ex), total resin (m_R), and different types of resin (m_A , m_C , m_P) dissolved vs. time for ethanol



condition of Eq. 17, Eq. 16 can be integrated to yield Eq. 18:

$$t = t_A, m_C = m_{C0} \quad (17)$$

$$m_{C0} - m_C = K'' \cdot S_C \cdot (t - t_A) \quad (18)$$

Now, it is necessary to consider that S_C changes with time, as Resin P is being dissolved and a new pore wall is exposed to the solvent:

$$\text{for } t < t_P, S_C = \pi \cdot d \cdot l \quad (19)$$

$$\text{for } t > t_P, S_P = \pi \cdot d \cdot l_T = S_C^T \quad (20)$$

Thus, substituting l , from Eq. 9, changing with t , and combining Eq. 12 and Eq. 18, the following equation is obtained, which is valid till $t = t_P$:

$$m_{C0} - m_C = K'' \cdot K' \cdot (\pi \cdot d / \rho) \cdot (t - t_A)^2 \quad (21)$$

From this moment, taking into account that $l = l_T$ is constant, and $m_P = 0$, the equivalent equation can be written as Eq. 22:

$$m_{C0} - m_C = K'' \cdot d \cdot l_T \cdot (t - t_A) \quad (22)$$

The final time at which all Resin C is dissolved is given by Eq. 23:

$$t_C = (m_{C0} / K'' \cdot \pi \cdot d \cdot l_T) + t_A \quad (23)$$

Application of the model

The model described above was applied with the following assumptions:

Wood geometry is assumed as shown in Table II. In these conditions,

for 2 kg of chips, the following values are obtained:

$$\text{Ducts: } 12.8 \times 10^4$$

$$S_A = 12.8 \times 10^4 \times 4.714 \times 10^{-4} = 60.34 \text{ cm}^2$$

$$S_P = 12.8 \times 10^4 \times 2.405 \times 10^{-4} = 30.78 \text{ cm}^2$$

$$S_C^T = \pi \cdot d \cdot l_T = 2815 \text{ cm}^2$$

Approximately 50% of the total extract is resin, from which only 2% is Resin A, 50% is Resin P and 48% is Resin C. For 2 kg of chips, the distribution assumed is:

- Total extract: 53 g, composed of 26.5 g of resin and 26.5 g of other extract
- Resin A: 2% resin $\cong 0.53 \text{ g}$ ($= m_{A0}$)
- Resin P: 50% resin $\cong 13.25 \text{ g}$ ($= m_{P0}$)
- Resin C: 48% resin $\cong 12.72 \text{ g}$ ($= m_{C0}$).

The amount of Resin P can be also calculated taking into account the pore volume ($S_P \times l = 12.158 \text{ cm}^3$) and resin density ($\rho = 1.084 \text{ g/cm}^3$), which yields an amount of Resin P of 13.18 g (very close to the one calculated above).

The free solubilization constant, K , was calculated for each solvent—propanone ethanol, trichloromethane, and diethylether—by the solution of pure resin. The values for these parameters are given in Table III, together with the calculation of t_A , according to Eq. 4. It can be seen that the values of m_{A0} and t_A are negligible compared with the amount and solubilization time of the other types of resin,

P and C. K' and K'' were calculated for the four solvents by nonlinear regression (6) to the experimental extract data according to Eqs. 24 and 25:

for $t < t_P$:

$$Ex = (1/0.5) \cdot \{m_{A0} + [K' \cdot (t - t_A)] \cdot [S_P + K'' \cdot (\pi \cdot d / \rho) \cdot (t - t_A)]\} \quad (24)$$

for $t > t_P$:

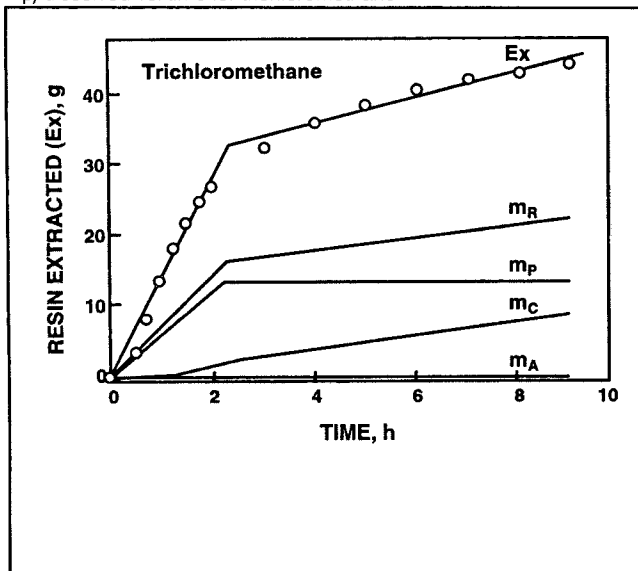
$$Ex = (1/0.5) \cdot \{m_{A0} + m_{P0} + K'' \cdot S_C^T \cdot (t - t_A)\} \quad (25)$$

With t_P calculated according to Eq. 13. K' and K'' values are given in Table IV, together with the confidence interval for 95% probability.

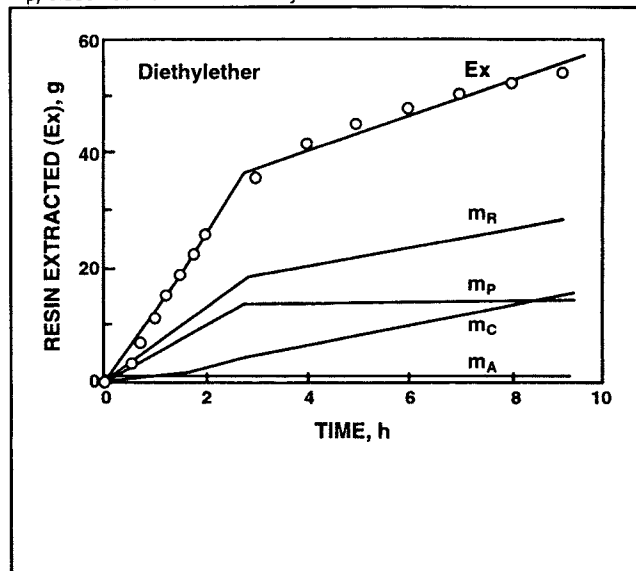
Discussion

When ethanol is used as solvent, the K'' value is not significantly different from zero, with a probability of 95%, because the upper and lower values are respectively positive and negative. The explanation of this fact can be that ethanol is not able to attack the epithelial cells, and the resin inside these cells is not dissolved. Fitting again the experimental results obtained with ethanol, and taking into account only the solubilization of Resins A and P, a value for K' of $0.149 \times 10^{-4} \text{ g/cm}^2 \cdot \text{s}$ (between 0.142 and 0.157×10^{-4} at a 95% probability level) was calculated. Figures 4-7, one for each solvent, show the comparison between experimental and theoretical results. They show good agree-

6. Extract (Ex), total resin (m_R) and different types of resin (m_A , m_C , m_P) dissolved vs. time for trichloromethane



7. Extract (Ex), total resin (m_R) and different types of resin (m_A , m_C , m_P) dissolved vs. time for diethylether



ment between experimental data and those given by the model. Figures 4–7 show the amount of each type of resin (A, P, and C) solubilized with time, according to the model calculation.

The values calculated for K' for the different solvents show that if a constant value of the mass transfer coefficient, K'_L , is assumed, the saturation concentration, C_R^e , must be high for trichloromethane and propane, somewhat smaller for diethylether, and much smaller for ethanol. Nevertheless the mass transfer coefficient from the cells, K'' , through the membrane definitely demonstrates the highest value for diethylether, with a smaller for trichloromethane, and an even smaller value for propane, being zero for ethanol□.

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Nomenclature

C	= concentration of resin	S	= surface
D	= diffusion coefficient of the resin in the pore	t	= time
D'	= diffusion coefficient through the cell membrane	t_A, t_C, t_P	= times of total solubilization of A, C and P resins
E	= cell depth	ρ	= resin density
Ex	= total amount of extractives, resin + other	Subscripts	
K	= free solubilization coefficient	A	= relative to resin A
K', K''	= rate constants of resin solubilization, for P and C resin types	C	= relative to resin C
K_L	= mass transfer coefficient of Resin P to bulk solvent	0	= initial value
K'_L, K''_L	= overall mass transfer coefficients of Resin P and C	P	= relative to resin P
l	= axial position of Resin P inside the pore	R	= relative to total resin
l_L	= total length of the pores	Superscripts	
m	= amount of resin	e	= saturation value
r	= radial position between pore and duct, inside the cells	T	= denotes total or constant value
R_c	= dissolution rate of Resin C		