

Kinetics of wood extraction with solvents

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ABSTRACT *Wood extraction was studied with diethylether, dimethylbenzene, ethanol, methylbenzene, propanone, and trichloromethane used as solvents. Based on the observations at both laboratory and pilot plant scale, a kinetic model is proposed for the extraction process. The model consists of three steps: (a) solubilization of rosin at easily accessible surface sites, (b) solubilization of less accessible sites following diffusion of the solute into the wood pores, and (c) solubilization of intracellular rosin accessed via osmosis or rupture of cell membranes. The model is used to explain experimental differences between strong and weak solvents.*

KEYWORDS

Ethanol
Extractives
Pulping
Rosin
Solvents

Minor components of wood are chemicals which would be able to be used in the industry if their quality and concentration were high enough and their price low enough. These chemicals can be extracted from wood, but treated wood must also be capable of being used for pulp and paper production if a commercial application is required. In a previous work (1), the main extracted products, their quality, and the availability of the treated wood for pulp and paper production have been shown. In this way, wood extraction would be an inexhaustible source of chemicals such as turpentine and fatty and rosinic acids (2).

The design of the extraction installations makes necessary the knowledge of the extraction rate and its relationships with operational conditions. The kinetic laws for the extraction rate depend on the complex internal structure of wood (3). Some authors (4, 5) have proposed to destroy this structure by mechanical grinding, thereby increasing the yield in extraction. This size reduction has two main effects:

1. A significant change in the internal structure of the chip wood. The grinding destroys the body of the wood, becoming the so-called "milled" wood.
2. An internal surface increasing for weight unit. As a consequence, a significant increase in the available wood surface opened to the solvent action is achieved.

Nevertheless, this size reduction decreases the wood quality for pulp and paper production (6).

The aim of this work is to study the kinetics of wood extraction. The kinetic model must take into account the different nature and extraction power of the different solvents to be used and the influence of the main variables, such as the particle size of wood. For building the kinetic model, it will be necessary to take into account the different steps followed in the solubilization of the minor components of wood, in which the internal structure must play an important role.

Experimental procedures

Experimental data were obtained at the laboratory and on the pilot plant scale.

Pilot plant

The pilot plant installation was described in a previous article (1). Briefly, the extractor is a 20-L stainless steel vessel with a basket inside that can hold up to 3 kg of chips. The extractions are carried out in batches. The sample collection and the analysis were also described earlier (1).

Laboratory

Laboratory extractions were carried out in 1-L Erlenmeyer flasks containing 0.8 L of solvent and 40 g of wood chips of a determined size. Experiments were performed in batch mode for both solvent and wood chips. The flasks were constantly agitated during the extraction. At a predetermined time, the contents of the flasks were filtered by Buchner funnels and porous glass. The excess solvent was distilled off, and the wood chips were dried at 100–105°C.

I. Extractives content using different solvents

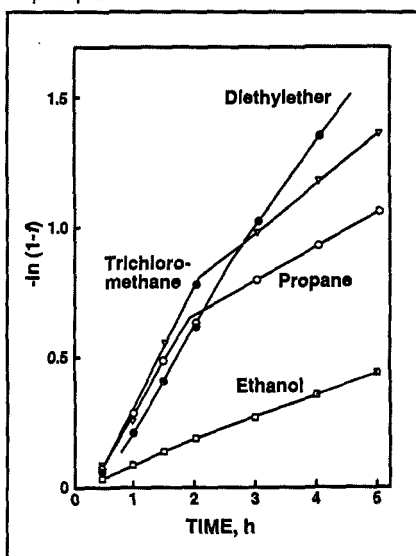
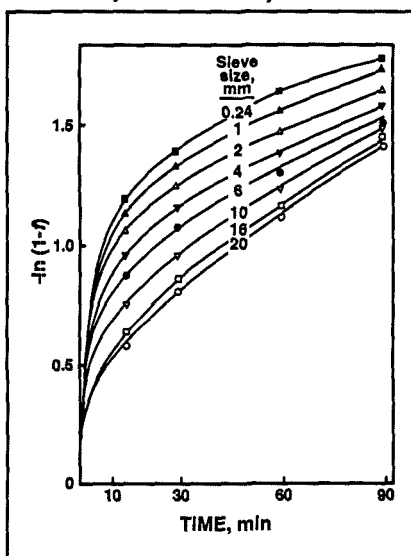
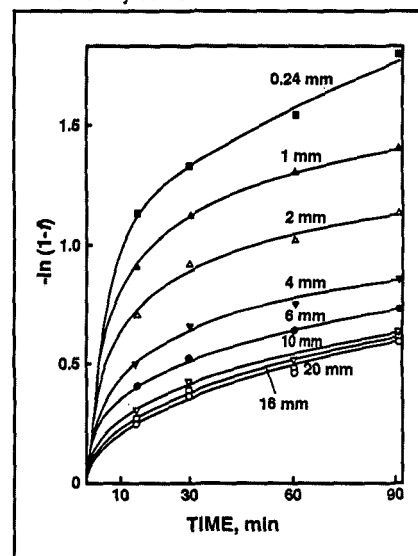
Solvent	Extracted, % on o.d. wood
Diethylether	2.73
Dimethylbenzene	2.71
Ethanol	2.60
Methylbenzene	2.79
Propanone	2.61
Trichloromethane	2.57

TAPPI T 204.

II. Experimental results at the pilot plant scale: extracted rosin fraction over time using propanone, trichloromethane, diethylether, and ethanol

Time, min	Propanone	Trichloromethane	Diethylether	Ethanol
15	0.01	0.01	0.02	0.01
30	0.07	0.06	0.06	0.03
60	0.25	0.26	0.20	0.08
90	0.39	0.43	0.34	0.13
120	0.47	0.52	0.47	0.17
180	0.55	0.63	0.64	0.24
240	0.61	0.69	0.74	0.30
300	0.65	0.74	0.81	0.36
360	0.69	0.79	0.87	0.41
420	0.73	0.82	0.91	0.45
480	0.76	0.85	0.95	0.50
540	0.78	0.88	0.97	0.54

Chip size of 21 mm.

1. Variation of $-\ln(1-f)$ vs. time for the results at pilot plant scale2. Variation of $-\ln(1-f)$ vs. time for the results at laboratory scale with diethylether as solvent3. Variation of $-\ln(1-f)$ vs. time for the results at laboratory scale with ethanol as solvent

Pinus pinaster wood was used in all the runs. Only one size, 21 mm, was used at the pilot plant scale, but different sizes were used at the laboratory scale. The different chip sizes were obtained by cutting the wood in a blade disc cutter, then grinding them in a hammermill. The different sizes obtained are indicated by the size of the sieve opening (in mm) in which they were retained. Thus, eight different sizes of sieves were used: 20, 16, 10, 6, 4, 2, 1, and 0.24 mm. Chips larger than 20 mm and smaller than 0.24 mm were rejected. All the chips were conditioned under a controlled

atmosphere at 20°C and 60% RH and were stored in plastic bags.

The solvents studied and the TAPPI extracts are listed in Table I.

Experimental results

Pilot plant

The results obtained at pilot plant scale, together with the experimental procedure, were presented previously (1). A summary of these results is presented in Table II, as the rosin fraction extracted for a constant chip size of 21 mm.

Laboratory

The results in the laboratory were obtained at different wood particle sizes. The weight of rosin extracted from 40 g of wood was measured, and the fraction of the rosin extracted was determined based on the TAPPI extract from Table I. Table III shows the results of the rosin fraction extracted over time with different solvents and for several particle sizes.

Interpretation of the results

The results obtained in the laboratory using chips of various sizes support

III. Experimental results in wood extracted with different solvents

Time, min	Sieve size, mm							
	20	16	10	6	4	2	1	0.24
<u>Propanone</u>								
15	0.48	0.51	0.56	0.60	0.64	0.67	0.69	0.71
30	0.54	0.57	0.61	0.67	0.69	0.72	0.74	0.75
60	0.63	0.65	0.69	0.72	0.72	0.75	0.76	0.78
90	0.71	0.73	0.75	0.76	0.77	0.78	0.79	0.79
<u>Trichloromethane</u>								
15	0.33	0.36	0.43	0.49	0.53	0.58	0.61	0.63
30	0.34	0.37	0.44	0.50	0.54	0.59	0.63	0.65
60	0.45	0.48	0.53	0.58	0.61	0.65	0.67	0.68
90	0.51	0.53	0.56	0.59	0.63	0.67	0.69	0.71
<u>Diethylether</u>								
15	0.44	0.47	0.53	0.58	0.61	0.65	0.68	0.69
30	0.53	0.56	0.61	0.66	0.68	0.71	0.73	0.74
60	0.67	0.68	0.70	0.72	0.74	0.77	0.79	0.80
90	0.75	0.76	0.77	0.77	0.79	0.80	0.82	0.83
<u>Ethanol</u>								
15	0.23	0.20	0.26	0.34	0.39	0.49	0.58	0.68
30	0.34	0.35	0.36	0.43	0.48	0.60	0.68	0.73
60	0.37	0.38	0.40	0.47	0.53	0.63	0.73	0.78
90	0.45	0.45	0.47	0.52	0.58	0.68	0.75	0.83
<u>Methylbenzene</u>								
15	0.17	0.17	0.17	0.17	0.18	0.22	0.29	0.41
30	0.20	0.20	0.20	0.21	0.22	0.26	0.33	0.48
60	0.24	0.24	0.24	0.25	0.27	0.32	0.40	0.53
90	0.27	0.27	0.28	0.30	0.34	0.41	0.49	0.60
<u>Dimethylbenzene</u>								
15	0.15	0.16	0.18	0.23	0.27	0.34	0.40	0.48
30	0.17	0.19	0.23	0.28	0.33	0.40	0.46	0.52
60	0.24	0.25	0.28	0.32	0.37	0.44	0.54	0.58
90	0.29	0.30	0.33	0.37	0.42	0.48	0.54	0.59

those results obtained earlier at the pilot plant. The extracted rosin fraction increased with time and increased when the particle size of the wood decreased.

Propanone and diethylether yielded higher fractions after 15 min of extraction, but diethylether presented the greatest yield in extraction products after 90 min. The yield from ethanol extraction was modest after short extractions of large particles, but it increased as extraction time increased and particle size decreased. Ethanol extraction was comparable to that of diethylether after 90 min of

extraction of the smallest particles. This finding is probably the result of ethanol's ability to solubilize some wood components that are not affected by other solvents. This capacity of ethanol may be attributed to its high polarity.

The benzene derivatives, methylbenzene and dimethylbenzene, extracted the smallest amounts of rosin. As with the other solvents tested, the amount of rosin extracted by the benzene derivatives increased as the extraction time increased and the particle size decreased.

Kinetics of wood extraction

The data from wood extraction may be best described with a model similar to that used previously for the extraction of wood sugars (7). The extraction rate of rosin can be considered to follow a first-order model with respect to the nonextracted rosin and can be expressed as:

$$r = df/dt = k(1-f) \quad (1)$$

where f is the rosin fraction extracted. This equation, with the boundary condition $f = 0$ at $t = 0$, integrates to

$$-\ln(1-f) = kt \quad (2)$$

Analysis of pilot plant data with the kinetic model

Part of the data listed in Table II were transformed with Eq. 3 and are plotted in Fig 1. The points of each plot are best fitted by two straight lines, with the early line having the greater slope. This finding agrees with the results of others (8).

Table IV lists the values of k obtained from the pilot plant results at time intervals greater and less than 2 h.

Analysis of laboratory data with the kinetic model

The results obtained in the laboratory (Table III) resemble those found at the pilot plant scale when the data are transformed with Eq. 3. Figures 2 and 3 are representations of the results obtained, with diethylether and ethanol as examples. As can be seen, the slopes of the curves decrease and approach linearity over time. Linear slopes indicate a constant k value, and linearity was approached more quickly when larger particles were used.

Table V lists the values for k obtained from different particle sizes with the different solvents. These values are the average of k values found after 60 min and 90 min of extraction, and they represent k values found on the linear part of the slopes indicated in Figs. 2 and 3. The values of k depended on the chemical nature of the solvent employed. For the stronger solvents (such as propa-none, trichloromethane, and diethylether), the value of k decreased when the particle size decreased. For chip sizes between 2 mm and 0.24 mm, values of k were in the range of those found at pilot plant scale at times exceeding 120 min. By contrast, for the weak solvents (ethanol and the benzene derivatives), the k values were almost constant for all particle sizes 1 mm and larger; values of k increased at the smallest size.

Discussion

The change in the value of k with both time and particle size may result for several reasons:

- A decrease in the active surface
- A change in the controlling, or rate-determining, step of the extraction process

IV. Values of k for the pilot plant results for two time intervals of less than and greater than 2 h

Time, min	Propa-none	Trichloro-methane	Diethyl-ether	Ethanol
< 120	0.0071	0.0082	0.0069	0.0019
> 120	0.0020	0.0030	0.0056	0.0014

Sieve size = 21 mm.

- A change in the chemical nature of the extract products.

This last explanation was suggested by Anderson (9) and can be rejected in light of the results reported in a previous work (1). In that study, we found that the chemical nature of the extracted products did not change appreciably either with time or with the different solvents used.

The most reasonable explanation involves a change in the rate-determining step of the extraction process. The current data suggest that there are three major stages in the extraction process:

1. The solvents initially act on the most accessible solute sites found on the chip surface. At this stage, the rate-determining step is either the mass transfer of liquid to solid or the dissolution rate of the solvents.
2. After this surface material is dissolved, the rate-determining step becomes the diffusion of the solvent into the wood pores (rosinic canals and wood radii) to find other less accessible soluble materials.
3. The solvent must reach the minor components in the wood epithelial cells by osmosis or after the rupture of cell membranes.

This final step would explain the observation by Hadgglun (10) that pinosilvine cannot be extracted with ether unless the wood has been treated previously with ketone, even though pinosilvine is highly soluble in ether.

According to this hypothesis, wood rosin extraction can be represented by the diagram shown in Fig. 4. The OABC line represents the extraction

process with stagnant fluid. In this case, only two sections of the line exist because the rates of the Steps 1 and 2 are equal. If the flow rate of the fluid increases, the line changes from OABC to ODEF, as a result of the increase of the rate coefficient k' of Step 1. The upper limit of this step is represented by the line ODGH. Here, solvent flow is at a maximum, and the rate of the step is limited by the dissolution of the rosin. Under these conditions, the position of data lines falling in the region of the diagram between the OABC and ODGH lines is determined by the particle size; lines move from OABC toward ODGH as particle size decreases.

The time necessary to complete the first step, t' , decreases as the flow rate of the fluid increases. The length of t' increases as the particle size decreases because the quantity of easily accessible wood increases.

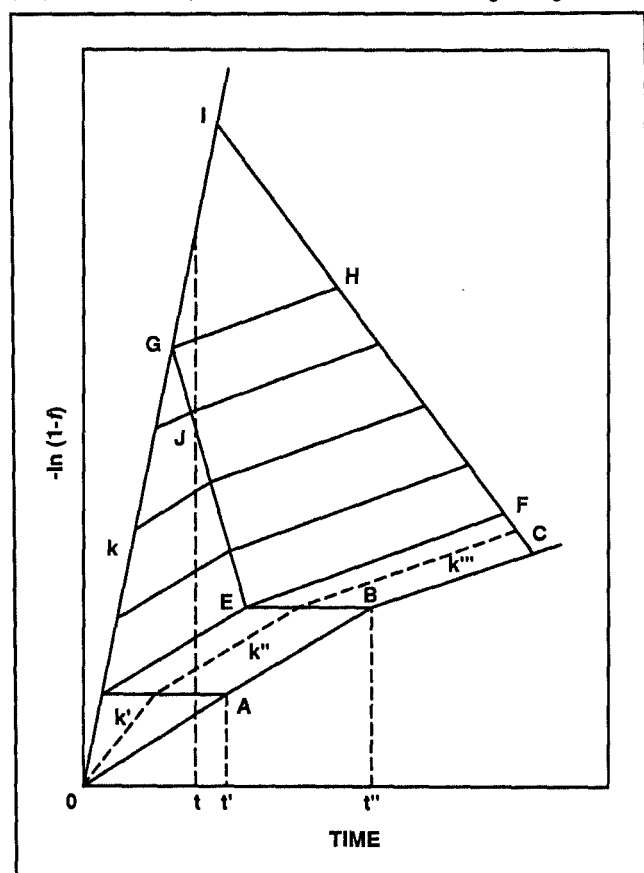
The period of time between t'' and t' , during which Step 2 controls the process rate, decreases as the particle size decreases. The reduction of this time period is due to the disappearance of the internal structure of the wood particles, resulting in a more rapid onset of Step 3. The Point G represents the elimination of the internal structure as a factor, and only Steps 1 and 3 have to be considered. If the size reduction is continued, even the epithelial cells can be destroyed, and all of the rosin becomes readily accessible to the solvent. This situation is represented by Point I.

Therefore, if the operational conditions are such that the operation is under the line ODEF, it is possible to decrease the time t' by increasing the fluid flow rate. Once Point D is reached, only the size reduction of the

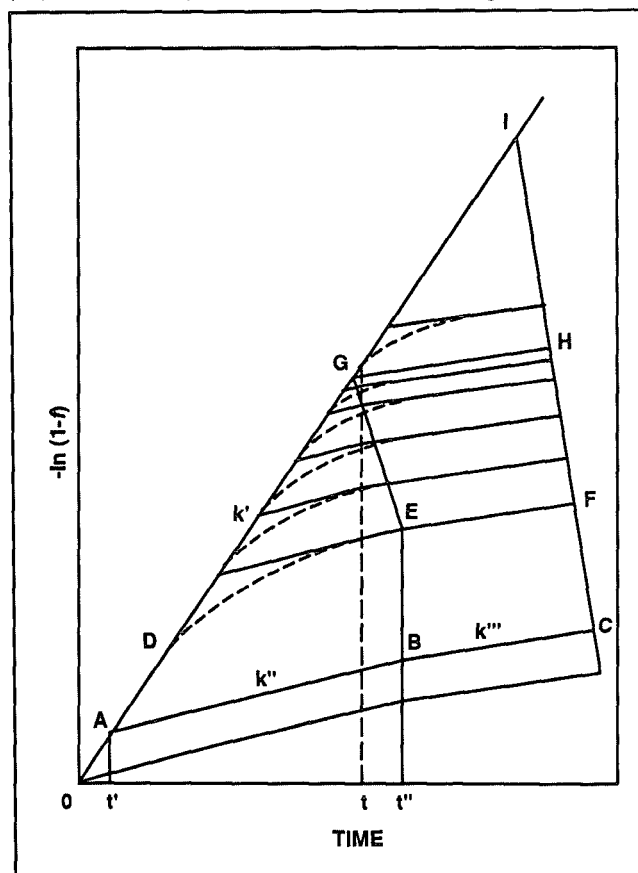
V. Values of k for the laboratory results at a time interval of 60–90 min

Sieve size, mm	Propane	Trichloromethane	Diethylether	Ethanol	Methylbenzene	Dimethylbenzene
20	0.0078	0.0041	0.0107	0.0031	0.0021	0.0027
16	0.0075	0.0040	0.0100	0.0030	0.0021	0.0025
10	0.0073	0.0045	0.0085	0.0029	0.0021	0.0023
6	0.0058	0.0045	0.0069	0.0029	0.0023	0.0023
4	0.0050	0.0043	0.0065	0.0034	0.0028	0.0024
2	0.0040	0.0041	0.0057	0.0037	0.0036	0.0025
1	0.0035	0.0036	0.0057	0.0046	0.0036	0.0026
0.24	0.0015	0.0032	0.0046	0.0053	0.0050	0.0027

4. Change of k values during the extraction process according to the proposed three-step model for wood extraction using strong solvents



5. Change of k values during the extraction process according to the proposed three-step model for wood extraction using weak solvents



wood chip is able to increase the extraction yield.

Some of the experimental results can be explained according to the three steps considered for the extraction. First, the rosin fraction extracted in the laboratory was greater than that extracted in the pilot plant when similar particle sizes were used (21 and 20 mm, respectively). This difference can be attributed to the more turbulent flow of the solvent in the laboratory.

The rosin fractions obtained at shorter extraction times were similar for every particle size for all solvents. These results were found because the process rate at short extraction times is determined by the rate of the first step, which is not a function of the chip size.

The values of k in the second period of time ($t > 120$ min) in the pilot plant were in the range of those obtained in the lab after long extraction times ($60 > t > 90$ min) using the smallest

particle size, 0.24 mm. The similarity of k values can be explained on the basis that the period of time of the second step, $t'' - t'$, decreases as the particle size decreases, thereby rendering Step 3 control of the process rate. In this situation, neither the fluid flow rate nor particle size influence the process rate.

These observations were not made for the weaker solvents (ethanol and benzene derivatives). With these

solvents, the k value increased with the smaller particle sizes. This finding can be accounted for by the smaller differences among the values of k' , k'' , and k''' and the gradual change from one step to another. This situation is represented by the drop lines in Fig. 5. Thus, the slope of the curves at any time t can increase as particle size decreases. At greater time with this type of solvent, the value of k must decrease until values correspond to k values of Step 3, as was found at the pilot plant scale. □

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