

Displacement washing of softwood pulp cooked to various levels of residual lignin content

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ABSTRACT: This study investigates the influence of the degree of delignification of kraft spruce pulp cooked at seven different kappa numbers, ranging from 18.1 to 50.1, on the efficiency of displacement washing under laboratory conditions. Although the pulp bed is a polydisperse and heterogeneous system, the correlation dependence of the wash yield and bed efficiency on the Péclet number and the kappa number of the pulp showed that washing efficiency increased not only with an increasing Péclet number, but also with an increasing kappa number. The linear dependence between the mean residence time of the solute lignin in the bed and the space time, which reflects the residence time of the wash liquid in the pulp bed, was found for all levels of the kappa number. Washing also reduced the kappa number and the residual lignin content in the pulp fibers.

Application: Of the basic brownstock washing operations, displacement washing is the most important and effective mechanism, and washing equipment is designed with emphasis on it. The information in this paper will enrich resources related to pulp washing that can impact end-product quality.

The pulp washing operation is a very crucial and important unit operation occurring after the cooking of wood materials in pulp production. Efficient washing reduces the additives load and oxidizable precursors in the bleaching operation. Moreover, inefficient washing negatively affects all of the following operations in the mill, including the quality of the finished products [1].

Pulp washing involves three basic operations: dilution, extraction, and displacement. Considering the same amount of wash liquid, displacement washing is more effective than washing based on dilution followed by thickening. The displacement washing of kraft pulp has been investigated by several researchers based on different points of view [2–10]. Although brownstock contains many chemical compounds, the amount of lignin present in the washed pulp or effluent liquid determines the washing efficiency.

Many variables have been studied for removal of the maximum amount of lignin using the minimum amount of wash liquid to obtain high washer efficiency. Physical characteristics of the fibers and pulp bed are considered to play the most important role in displacement washing. Pulp fibers are highly heterogeneous and compressible. The well-investigated variables related to washing efficiency are dilution factor [4,11], pulp bed consistency, pulp bed thickness, wash liquid velocity, and temperature of wash liquid [6,12–15]. Disagreements over the experimental results for the same variable were observed. Both the positive and negative influence of pulp bed consistency have been observed in studies by different authors [6,12,15]. It is obvious that temperature affects the mobility of the displacing and dis-

placed liquids. The displacement washing efficiency has a linear relationship with the temperature [2,11]. However, Trinh et al. [6] disagreed and claimed temperature has no effect on displacement washing efficiency.

Although both softwood and hardwood belong to vascular plants, their chemical and morphological properties are different. The most noticeable chemical difference in the lignocellulosic materials is seen in the content and composition of lignin. The softwood has higher lignin content than hardwood. The compositional differences of wood materials influence the brownstock washing efficiency. It has been observed that the concentration of lignin in the bed influences the wash yield efficiency. High initial lignin concentration in the softwood pulp fibers reduces the wash yield; however, lower initial lignin concentration in hardwood pulp fibers shows higher wash yield [9,16]. The presence of lignin in pulp depends on the delignification of wood material during the pulping operation. However, little effort has been devoted to investigating the influence of chemical composition of the pulp, especially lignin content, upon the displacement washing efficiency.

In pulp mills, the kraft process is used to produce pulp fibers at varying degrees of delignification. Higher kappa number softwood pulps are produced for packaging grades, and these fibers are generally not bleached. Lower kappa number pulps are produced for bleachable grade end products. Therefore, it is useful to know the washing effectiveness of pulp with varying degrees of delignification, simply because imperfect washing generally leads to inefficiencies in subsequent fiber processing such as in-

Pulp	κ	l_A , mm	l_w , mm	FC , mg m ⁻¹	l_w/l_A	$a_v \times 10^{-5}$, m ⁻¹	ρ_P , kg m ⁻³
Spruce	18.1	1.91	2.77	0.103	1.45	1.76	125–148
	19.6	1.94	2.76	0.126	1.42	1.84	124–143
	22.8	2.01	2.80	0.104	1.39	2.15	123–129
	32.3	1.88	2.68	0.123	1.43	2.05	121–129
	37.0	1.87	2.65	0.125	1.42	2.08	124–129
	44.4	1.75	2.52	0.128	1.44	2.19	122–125
	50.1	2.09	2.84	0.111	1.36	2.54	127–136
Beech [18]	31.6	0.36	0.63	0.403	1.75	3.10	110–120

κ = kappa number of pulp before displacement washing; l_A = arithmetic average length of fiber; l_w = weighted average length of fiber; FC = fiber coarseness; a_v = specific surface of fibers; ρ_P = bed consistency.

I. Geometrical properties of the kraft pulp.

creased chemical usage in bleaching, for example. Thus, our results could provide additional data on the washing of kraft pulps with various degrees of delignification and at the same time confirm that the washing process is a complicated one influenced by many factors characteristic of a porous fiber system.

This paper deals with the influence of degree of delignification of softwood pulp on the displacement washing efficiency in terms of wash yield, the Péclet number, bed efficiency, and mean residence time and space time.

EXPERIMENTAL

The kraft pulp used for the displacement washing experiment was produced from spruce wood chips collected from an industrial source and stored under laboratory conditions. The undesirable particles, such as oversized chips, bark, and knots, were sorted out in accordance with the TAPPI Standard Test Method T 265 “Natural dirt in wood chips.” The basic dimensions of the chips were within the limits of 20 mm < length < 59 mm; 10 mm < width < 30 mm; and 1.6 mm < thickness < 8.4 mm. The moisture content of the chips was measured separately before each batch of the cooking experiment. The batch kraft pulping was performed with a laboratory rotary digester having six stainless steel cylindrical cooking vessels of 0.75 L capacity, immersed in an oil bath.

The cooking conditions, when the rejects amount was acceptable, were as follows: material-to-liquor ratio of 1:4 and active alkali charge of 18 mass% as sodium oxide (Na₂O) on oven-dry wood mass. Industrial white liquor, at a sulfidity of 28%, was used. The temperature regime was as follows: 45 min heating to 110°C, with 45 min dwell time at this temperature; 60 min heating to cooking temperature ranging from 162°C to 168°C; and then dwelling at cooking temperature to achieve the desired H-factor. The spruce wood was cooked at seven different levels of H-factor,

namely, 3188, 2650, 1604, 1023, 842, 652, and 558 h corresponding to 18.1, 19.6, 22.8, 32.3, 37.0, 44.4, and 50.1 kappa number, respectively, determined for pulp according to TAPPI Test Method T 236 om99 “Kappa number of pulp.” The pulp was disintegrated with a laboratory Lorentzen & Wettre (Stockholm, Sweden) disintegrator, washed with tap water by dilution/thickening, screened manually using a 10 mesh sieve, dewatered to 30% consistency using a laboratory centrifuge machine, and stored in a refrigerator at 8°C.

The length of the pulp fibers was determined using a Kajaani FS-100 fiber analyzer (Valmet; Espoo, Finland). The effective specific surface of the fibers was determined from the volumetric flow of wash liquid at various consistencies of the bed at different pressure drops according to Ingman-son [17]. The geometrical properties of the pulp fiber are shown in **Table I**.

Displacement washing experiments with the pulp bed simulated under laboratory conditions were performed in a cylindrical glass tube that was 125 mm high with an inside diameter of 35 mm under constant bed height of 30 mm. The pulp beds were formed from a dilute suspension of about 3.7% of unbeaten unbleached kraft spruce pulp in black liquor. The black liquor used in the displacement washing, which was produced after softwood cooking, was obtained from the pulp mill. The solids content of the liquor was determined according to TAPPI Test Method T 211 “Ash in wood, pulp, paper and paperboard: combustion at 525°C,” and alkali lignin concentration was measured using a Cintra 10e ultraviolet spectrophotometer (GBC Scientific Equipment; Hampshire, IL, USA) at a wavelength of 295 nm. The properties of black liquor were as follows: solids content of 20.6 mass% (of which ash represented 60.7% and organic substances represented 39.3%); density of 1100 kg m⁻³ at 25°C; pH value of 12.6; and alkali lignin concentration of 56 kg m⁻³. No mechanical treatment was done during washing, constant bed height was

maintained using a permeable septum and a piston, and washing was carried out as prepared.

Distilled water at a temperature of 25°C that was used as a wash liquid was uniformly passed through the piston to the top of the bed at a constant pressure drop of 7 kPa. The washing effluent was sampled as soon as the wash liquid started to pass through the bed at different time intervals until the effluent was colorless. The collected samples were analyzed for alkali lignin concentration using the Cintra 10e ultraviolet spectrophotometer at a wavelength of 295 nm. The details of displacement washing experiments with pulp fibers, as well as the washing equipment, were described earlier [19]. In order to determine the permeability and average porosity of the experimented pulp bed, the volumetric flow rate of the wash liquid was gravimetrically measured at the same experimental pressure drop of 7 kPa after finishing the displacement washing run. Twelve displacement washing runs were performed at each kappa number level.

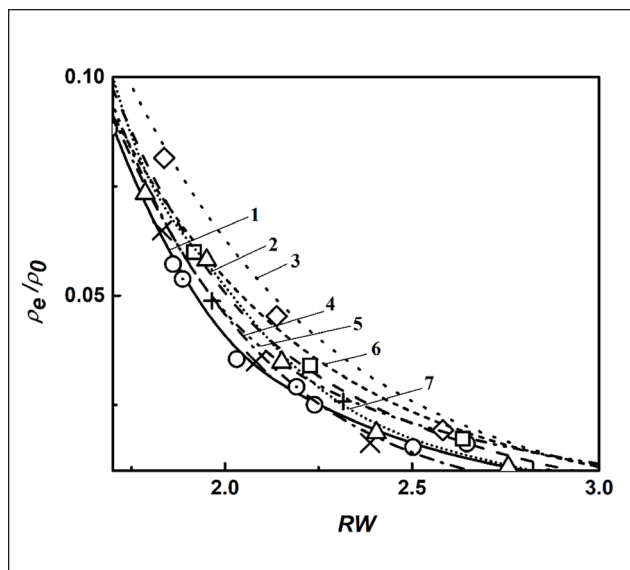
The residual lignin content of the pulps was measured before and after displacement washing. Klason lignin content in the sample was determined according to the TAPPI T 222 om-02 “Acid-insoluble lignin in wood and pulp,” and acid-soluble lignin was determined using the Cintra 10e ultraviolet spectrophotometer at a wavelength of 295 nm.

RESULTS AND DISCUSSION

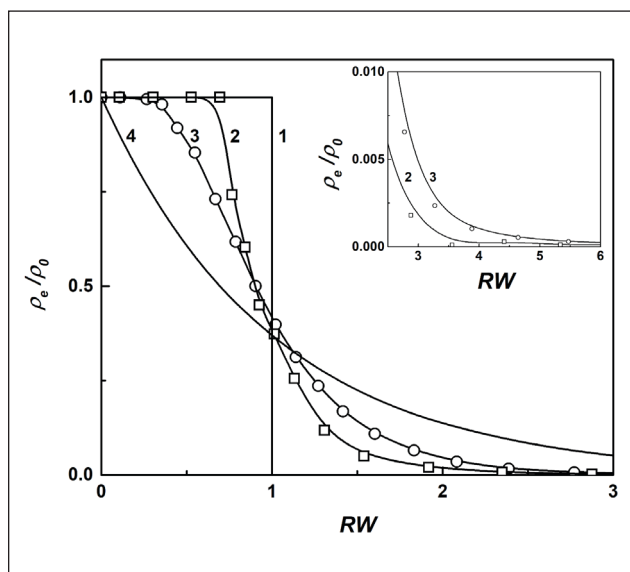
Displacement washing curve

The displacement washing experiments were described by the washing breakthrough curves produced from a response to a step change in concentration. The breakthrough curves, obtained in response to the output lignin concentration due to the input of wash liquid, showed a dependence in the dimensionless exit concentration of the lignin as ρ_e/ρ_0 against the wash liquor ratio, RW . The RW is ratio of the amount of wash liquid passed through the bed and the initial amount of mother liquor present in the bed. The displacement washing experiments were carried out with the kraft spruce pulp cooked to seven different degrees of delignification, as described by the kappa numbers given in Table I. The displacement washing curves for all the kappa numbers did not considerably differ. Therefore, only the segments of the breakthrough washing curves in the limits of the wash ratio ranging from 1.7 to 3.0, when the lignin leaching from the pulp fibers begins to show significantly, are demonstrated in **Fig. 1**. The small variation seems due to the physical difference of the pulp bed formation. However, all of the washing curves overlapped after the wash liquor ratio of 3.5.

A comparison of the breakthrough curves measured for the displacement of black liquor from the pulp bed formed from the kraft spruce pulp with a kappa number of 32.3 and the short-fibered kraft beech pulp [18] with the kappa number of 31.6 is demonstrated in **Fig. 2**. Both of the exit lignin concentration profiles are situated between plug flow



1. Displacement washing curves with dimensionless exit concentration of lignin from the pulp bed related to the wash liquor ratio of the kraft spruce pulps with the following kappa numbers: (1) 18.1 (○); (2) 19.6 (+); (3) 22.8 (◇); (4) 32.3 (×); (5) 37.0 (◊); (6) 44.4 (□); and (7) 50.1 (△).



2. Comparison of displacement washing curves with dimensionless exit concentration of lignin from the pulp bed against the wash liquor ratio: (1) plug flow; (2) beech pulp ($\kappa = 31.6$); (3) spruce pulp ($\kappa = 32.3$); and (4) perfectly mixed flow.

(curve-1) and perfectly mixed flow (curve-4). Based on the lignin concentration profile in the exit stream, the demonstrated washing curves in **Fig. 2** were apparently divided into four parts. The first part of the curve of the wash liquor ratio from 0 to about 0.3 was the displacement-dominated part of washing when the exit stream of the lignin concentration was the same concentration as the mother liquor. The washing profiles were the same in the first part. No sooner had the first part of the wash liquid passed through

the pulp bed than the exit lignin concentration dropped very rapidly. However, the second part of the curves from the wash liquor ratio of about 0.3 to 1 were considerably different; the washing curve for spruce pulp showed a comparatively flat profile of exit concentration of lignin compared with the beech pulp washing curve, which observed a more rapid change of exit lignin concentration. In the third part of the washing curve from $RW = 1$ to approximately 3.5, the exit lignin concentration profile was found flat in nature for both of the pulps. The diffusion mechanism was likely dominating in the third part of washing, which resulted in the flat profile of the washing curve. It was probably the result of the nature of the pulp bed, which could be characterized as an unmovable packing dumped randomly into the washing cell along with black liquor, occurring both in the void spaces and inside the fiber pores. It was assumed from Fig. 2 that the desorption and transportation of lignin from fiber wall to wash liquid was slower for the spruce pulp than for the beech pulp surface. The fourth section of the washing curves with the wash liquor ratio over 3.5 was fully controlled by the diffusional mechanism where both of the curves had approximately the same character. In this part of washing, the lignin adsorbed in the fiber lumen or fiber wall diffused to the wash liquid, and the nature of diffusion was independent of the type of pulp. Although the starting and ending nature of the two curves were almost the same, the difference before and after $RW = 1$ might be a result of the morphological and chemical compositional differences of the two varieties of pulp. The morphological properties of the material influence the pore size and the pore size distribution of the pulp bed, which affect the permeability [20].

The physical properties of the spruce pulp and the beech pulp fibers differed from each other, as demonstrated in Table I. Pulp fibers with less polydispersity are likely to form a more even pulp bed. However, the heterogeneity of the pulp bed increases with increasing length-to-diameter ratio of the fibers. It is generally known that spruce fibers have twice the length-to-diameter ratio of beech fibers, which resulted in a more heterogeneous pulp bed form than the kraft spruce pulp and showed lower efficiency in displacement washing. The heterogeneity of the pulp bed facilitates channeling and dispersion of solute during displacement washing. The comparatively flat profile of the breakthrough curve from spruce pulp washing indicated more dispersion of lignin in the wash liquid. The wash liquid passed through the open space, which is defined as the effective porosity of the bed, by displacing the dissolved solute. The effective porosity is the fraction of pore spaces in the bed open for wash liquid to flow. Effective porosity of the spruce pulp fiber bed was lower than that of the beech pulp bed, as shown in Table I. Lindsay [21] showed the permeability of a bed increased with increasing effective porosity. This phenomenon was reflected in the breakthrough curves showing the spruce pulp wash-

ing curve comparatively flat compared with that of the beech pulp washing curve.

Wash yield

The quality of the displacement washing of pulp is often expressed by the traditional wash yield, $WY_{RW=1}$, as follows:

$$WY_{RW=1} = \frac{\int_{RW=0}^{RW=1} \frac{\rho_e}{\rho_0} d(RW)}{\int_{RW=0}^{RW \rightarrow \infty} \frac{\rho_e}{\rho_0} d(RW)} \quad (1)$$

where ρ_e and ρ_0 refer to lignin concentration in the outlet liquor stream and initial mother liquor, respectively. The wash yield, $WY_{RW=1}$, is defined as the amount of solute washed out of the pulp bed at the wash liquor ratio equal to unity divided by the total amount of solute originally present in the bed.

The interfacial mixing between the displacing wash liquid and the displaced soluble materials is the main obstacle to achieving maximum efficiency in displacement washing. The Péclet number, Pe , is a dimensionless parameter used to describe the extent of dispersion of solutes that takes place in the displacing wash liquid [23,24]. The dimensionless Péclet number can be defined according to the following equation:

$$Pe = \frac{h u}{D \varepsilon} \quad (2)$$

where h is the height (or also thickness) of the pulp bed, u is the superficial velocity of the wash liquid, ε is the porosity of the pulp bed, and D is the dispersion coefficient. With respect to mass transport, the Péclet number is proportional to the ratio of the bulk mass flow to the dispersion mass flow [25]. The Péclet number indicates the level of dispersion of solute in the pulp bed. Arora et al. [26] showed that displacement washing with a lower Péclet number takes a longer time to obtain a steady state condition in comparison with the higher Péclet number. The Péclet number represents the back mixing of solute and deviation from the plug flow in the displacement washing system. If there is no adsorption of the solute observed on the particle surface, the Péclet number for the plug flow may approach infinity in the ideal case. On the other hand, the value is zero for the perfectly mixed flow system.

The washing experiments were finished at the wash liquor ratio equal to about 7 when the lignin concentration in the exit stream was about one thousandth of the initial lignin concentration in the pulp bed. The shape of the washing curves was described by the dispersion flow model, which contains a dimensionless parameter, the Péclet number, derived from the mass balance of the test

κ	Correlation Equation	δ , %	95% CI Coefficient	95% CI Exponent
18.1	$WY_{RW=1} = 0.720 Pe^{0.0550}$	1.55	0.709 – 0.731	0.0491 – 0.0608
19.6	$WY_{RW=1} = 0.741 Pe^{0.0389}$	1.34	0.729 – 0.752	0.0328 – 0.0451
22.8	$WY_{RW=1} = 0.705 Pe^{0.0583}$	1.18	0.700 – 0.710	0.0538 – 0.0629
32.3	$WY_{RW=1} = 0.706 Pe^{0.0603}$	0.56	0.703 – 0.709	0.0586 – 0.0621
37.0	$WY_{RW=1} = 0.725 Pe^{0.0473}$	1.48	0.716 – 0.735	0.0419 – 0.0528
44.4	$WY_{RW=1} = 0.695 Pe^{0.0733}$	1.77	0.683 – 0.707	0.0639 – 0.0826
50.1	$WY_{RW=1} = 0.749 Pe^{0.0410}$	1.18	0.738 – 0.760	0.0356 – 0.0464

κ = kappa number of pulp before displacement washing; δ = mean relative quadratic deviation; CI = confidence interval; $WY_{RW=1}$ = wash yield at wash liquor ratio of 1; Pe = Péclet number.

II. Correlation equations between wash yield and the Péclet number for washing of kraft spruce pulp at various kappa number levels.

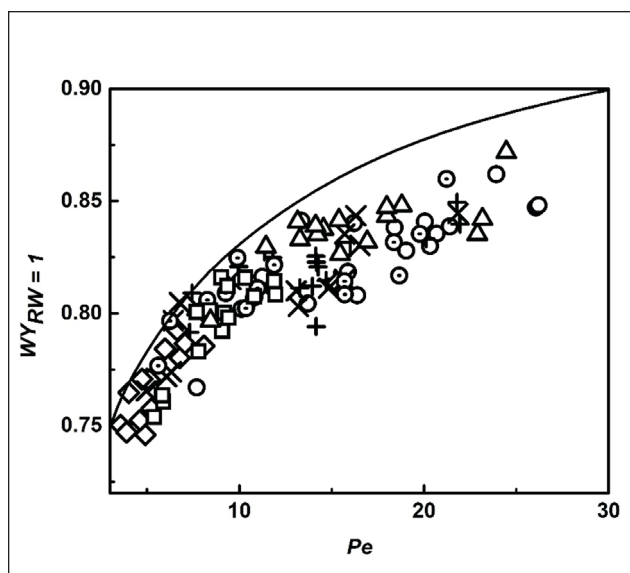
substance (lignin) for the given system in a non-continuous state. The Péclet number of all the experiments was calculated according to van der Laan [27].

The relationship between the wash yield at $RW = 1$ and the Péclet number was evaluated for all kappa number levels of the kraft spruce pulp. The correlation equations have been presented in **Table II**.

The cluster comparison of the kraft spruce pulp cooked to kappa numbers ranging from 18.1 to 50.1 is shown in **Fig. 3** in the interval of Péclet numbers ranging from 4 to 26 and with displacement wash yields between 0.75 and 0.87. Trinh et al. [6] reported the displacement wash yield of 0.87 for a kraft spruce pulp bed of 25 mm with a consistency of 125 kg m^{-3} at 30°C . From Fig. 3, it follows that almost all of the points were situated below the line deduced by Brenner [28] for non-porous particles where the displacement mechanism is not accompanied by the leaching of a solute from the particle walls. It was confirmed again that the wash yield for kraft spruce pulp depended upon the Péclet number to a small degree, similar to kraft hardwood [9,16] and soda rapeseed [10] pulps, as well as non-porous particles [28]. In order to express the effect of delignification degree of the kraft spruce pulps tested in our work, the mathematical treatment of all the experimental data gave the following correlation equation:

$$WY_{RW=1} = 0.643 Pe^{0.0773} \kappa^{0.0169} \quad (3)$$

with the mean relative quadratic deviation of the wash yield, δ , of 0.81% and the Akaike information criterion of -996. The 95% confidence intervals for the coefficient and for the power of the Péclet number and kappa number were (0.641; 0.645), (0.0767; 0.0779), and (0.0162; 0.0175), respectively. Hence, a satisfactory agreement was found between the experimental and the calculated data. From the overall relationship, it is seen that the wash yield increases with

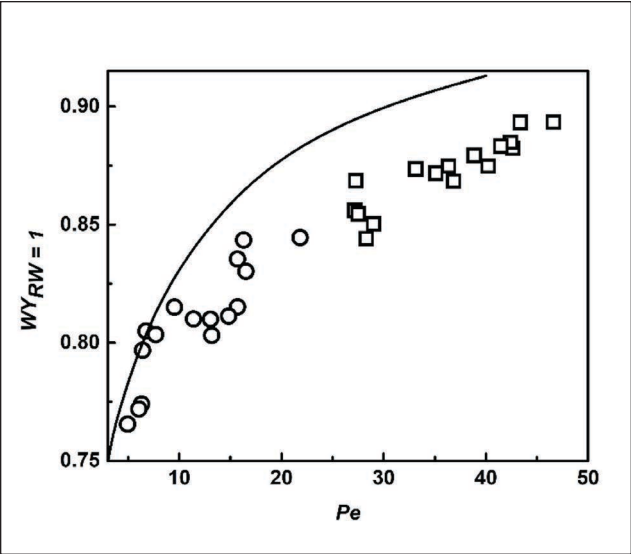


3. Wash yield as a function of the Péclet number for kraft spruce pulps with the following kappa numbers: (1) 18.1 ($\circ$); (2) 19.6 ($+$); (3) 22.8 ($\diamond$); (4) 32.3 ($\times$); (5) 37.0 ($\circ$), (6) 44.4 ($\square$); and (7) 50.1 ($\triangle$). Solid line according to Brenner [28].

increasing the kappa number of spruce pulp.

The comparative influence of the Péclet number on the wash yield for spruce pulp and beech pulp [18] washing with kappa numbers of 32.3 and 31.6, respectively, is shown in **Fig. 4**. In spite of the scatter in the data, it was evident that the wash yield slightly increased with increasing Péclet number for both spruce and beech pulps.

It was obvious that the data for the spruce and the beech pulp were located below the curve derived for the packed bed of non-porous particles by Brenner [28] (Fig. 4). This is presumably because, unlike the packed bed of non-porous particles, the displacement mechanism was reduced by prolonging the interfacial mixing between displaced and displacing fluids in the case of lignocellulosic fibers in the



4. Displacement wash yield as a function of the Péclet number: (○) spruce pulp, and (□) beech pulp. Solid line according to Brenner [28].

swollen state [25]. Between spruce and beech pulp, lower values for wash yield and the Péclet number were manifested for spruce pulp. It was mentioned that the spruce pulp formed a more heterogeneous bed, which facilitated the fingering or channeling phenomena. The channeling eased the wash liquid to pass through the bed without displacing the lignin present in the bed and at the same time, it helped lignin to disperse in the wash liquid. This might be one of the reasons for reducing the wash yield of spruce pulp. Moreover, Potůček [7] reported that the displacement wash yield decreased with increasing initial lignin concentration in the mother liquor. The initial alkali lignin concentration in the mother liquor was affected by the lignin content in the wood samples. It was found that the Klason lignin content of spruce wood was about 30.4 mass%, while

beech wood showed the lower lignin content of 24.5 mass% [16]. The mother liquor used in our study was evaluated for lignin concentration of 56 kg m⁻³. So, the lower values of the wash yield reported for spruce pulp can be also attributed to the higher initial alkali lignin concentration in contrast to 27 kg m⁻³ in the case of beech pulp [16].

Bed efficiency

The bed efficiency can be used as an important variable for comparing removal of solute (in our case alkali lignin) from the bed in the displacement washing process. Cullinan [29] derived a relationship for the efficiency of a pulp bed, *E*, the wash liquor ratio, *RW*, and the displacement ratio, *DR*, in the following form:

$$DR = 1 - \exp(-E \cdot RW)$$
 (4)

For the stationary pulp bed, the displacement ratio can be defined as follows:

$$DR = \frac{\rho_0 - \rho_{RW}}{\rho_0 - \rho_{WL}}$$
 (5)

where ρ_0 is the initial lignin concentration inside the pulp bed at *RW* = 0, and ρ_{RW} represents the average lignin concentration inside the pulp bed at any *RW*.

When the lignin concentration in the wash liquor ρ_{WL} = 0, and the initial and final consistencies are the same (meaning the liquor volume associated in the pulp bed has a constant value), then the displacement ratio is equal to the wash yield. Therefore, the bed efficiency is defined as:

$$E = -\frac{\ln(1 - WY)}{RW}$$
 (6)

The bed efficiency of the displacement washing for the

κ	Correlation Equation	δ , %	95% CI Coefficient	95% CI Exponent
18.1	$E_{RW=1} = 1.22 Pe^{0.146}$	4.02	1.17 – 1.27	0.131 – 0.161
19.6	$E_{RW=1} = 1.31 Pe^{0.104}$	3.56	1.25 – 1.36	0.088 – 0.121
22.8	$E_{RW=1} = 1.20 Pe^{0.136}$	2.68	1.18 – 1.22	0.126 – 0.146
32.3	$E_{RW=1} = 1.17 Pe^{0.154}$	1.25	1.16 – 1.18	0.150 – 0.158
37.0	$E_{RW=1} = 1.25 Pe^{0.125}$	3.99	1.20 – 1.29	0.110 – 0.139
44.4	$E_{RW=1} = 1.15 Pe^{0.178}$	4.19	1.10 – 1.19	0.156 – 0.200
50.1	$E_{RW=1} = 1.33 Pe^{0.115}$	3.33	1.27 – 1.38	0.100 – 0.130

κ = kappa number of pulp before displacement washing; δ = mean relative quadratic deviation; CI = confidence interval; $E_{RW=1}$ = wash yield at wash liquor ratio of 1; *Pe* = Péclet number.

III. Correlation equations between bed washing efficiency and the Péclet number for displacement washing of the kraft spruce pulp with different kappa number levels.

kraft spruce pulp, $E_{RW=1}$, was calculated by Eq. 6 at the wash liquor ratio equal to unity. The bed efficiency varies from 1 to ∞ for the perfect displacement process when the wash liquor ratio increases from 0 to 1. On the other hand, the bed efficiency is equal to unity for a perfectly mixed flow system. In practice, the displacement washing process is neither perfect displacement nor a perfectly mixed flow system [19]. In displacement washing, the dispersion of solute present in the bed to the wash liquid diminishes the bed efficiency. The extent of dispersion depends upon the properties of the packed bed and packing materials. The bed efficiency of the non-porous glass spheres, where displacement was the dominant mechanism at the interface of the displacing and displaced liquid, was higher than that of the pulp bed in which both displacement and diffusion mechanisms operate simultaneously [7].

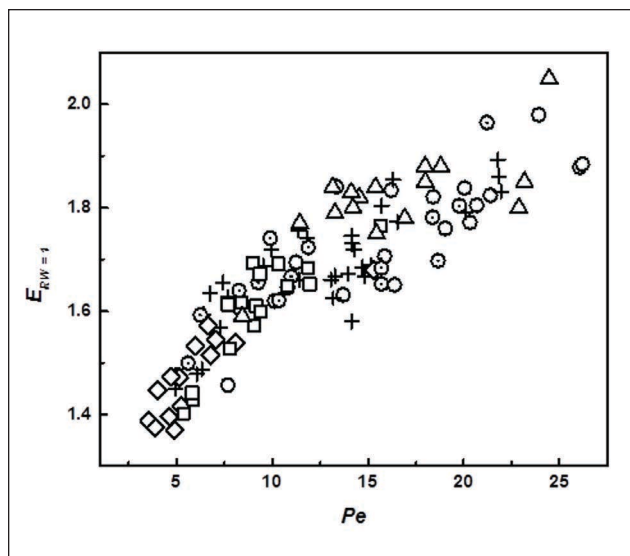
The bed efficiency was measured for the washing of kraft spruce pulp cooked to different kappa number levels. From our experimental data for individual kappa numbers, the dependence of bed efficiency was correlated to the dispersion parameter, the Péclet number. The correlation equations with mean relative quadratic deviation of bed efficiency and the regression coefficients and exponents with 95% confidence intervals are presented in **Table III**.

Although the results were scattered, the increasing trend of bed efficiency was observed with increasing the Péclet number. The effects of the Péclet number on the bed efficiency were not large at the individual kappa number level. However, significant effects of the Péclet number on the bed efficiency were observed for the earlier bed formed from glass spheres [7]. Unlike the glass spheres, the leaching of the lignin from the pulp surface to the wash liquid might play a major role in making the effect of the Péclet number insignificant.

The bed efficiency for the experiments at all kappa number levels of the kraft spruce pulp has been compiled in a plot as a function of the Péclet number in **Fig. 5**. An increasing trend in the bed efficiency with increasing Péclet number is obvious; however, the influence of the kappa number was unclear. Hence, the overall dependence of the bed efficiency on the Péclet number for washing of the kraft spruce pulp at all kappa number levels was derived in the following equation:

$$E_{RW=1} = 0.930 Pe^{0.196} \kappa^{0.0425} \quad (7)$$

with a mean relative quadratic deviation of bed efficiency, δ , equal to 2.37%, and the Akaike information criterion of -620. The 95% confidence intervals for the coefficient and for the power of the Péclet number and kappa number were (0.924; 0.936), (0.194; 0.197), and (0.0408; 0.0442), respectively. The correlation Eq. 7 derived over the same ranges of the Péclet number and kappa number as Eq. 3 revealed a relatively low effect of the kappa number on the bed ef-



5. Bed efficiency as a function of the Péclet number of kraft spruce pulp with various kappa numbers as follows: (1) 18.1 ($\circ$); (2) 19.6 ($+$); (3) 22.8 ($\diamond$); (4) 32.3 ($\times$); (5) 37.0 ($\square$); (6) 44.4 ($\square$); and (7) 50.1 ($\triangle$).

ficiency. It is worth mentioning that Potůček [7] also obtained an increasing trend in bed efficiency with increasing Péclet number for kraft pulp cooked from a blend of spruce and pine, ranging from 2.2 to 20 when the bed efficiency increased from 1.3 to 2.1.

Time parameters

Completion of washing at the shortest time possible is one of the prerequisites of efficient washing. Unlimited time is not allowed for carrying out the washing process due to the operating times for the preceding and following technological operations. The time required to pass through a porous pulp bed is one of the crucial parameters for describing displacement washing.

In displacement washing, two time parameters, including mean residence time of spent liquor and space time of the wash liquid, were considered for describing the washing efficiency. The mean residence time, t_m , which describes the total travelling time of solute in the bed, is defined as:

$$t_m = \int_{t=0}^{t=\infty} \frac{\rho_e}{\rho_0} dt \quad (8)$$

where t_m is the mean residence time of lignin in the pulp bed.

The space time, τ , is directly proportional to the void volume of the pulp bed, while the mean residence time is directly proportional to the total volume of the spent liquor present in the bed [16]. The space time describes the holding time of wash liquid in the pulp bed before leaving it. For a fixed length of pulp bed, the space time depends on

κ	Correlation Equation	r	ε
18.1	$t_m = 1.84 \tau$	0.94	0.42–0.50
19.6	$t_m = 1.77 \tau$	0.92	0.46–0.51
22.8	$t_m = 1.91 \tau$	0.91	0.31–0.43
32.3	$t_m = 1.78 \tau$	0.98	0.32–0.43
37.0	$t_m = 1.56 \tau$	0.93	0.47–0.52
44.4	$t_m = 1.66 \tau$	0.97	0.38–0.48
50.1	$t_m = 1.62 \tau$	0.98	0.43–0.56

κ = kappa number of pulp before displacement washing; r = correlation coefficient; ε = porosity of bed; t_m = mean residence time, min; τ = space time, min.

IV. Correlation of time parameters for displacement washing of the kraft spruce pulp with various kappa number levels.

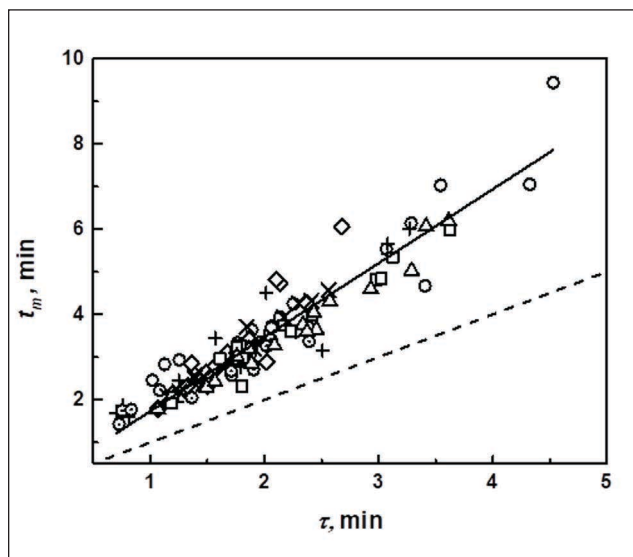
the bed porosity and wash liquid velocity, and it can be expressed as:

$$\tau = \frac{\varepsilon h}{u} \quad (9)$$

Lignocellulosic pulp fibers are highly compressible and their permeability of the bed depends on the bed porosity at the experimental consistency. The displacement washings of the kraft spruce pulps were carried out with overall consistency variation between 121 and 148 kg m⁻³ and a porosity variation from 0.31 to 0.56 (Table I). The space time characterizing the holding time of wash liquid is usually equal to the mean residence time of the solute if there is no sorption or diffusion on the surface of the bed material taking place, as it was earlier reported for the unmovable packing bed from glass spheres [7]. The mean residence time was always higher than the space time in pulp washing, because the lignin diffused from the surface of the fibers in the course of washing [7,8]. Hence, it was found from our experiments that the mean residence time was always higher than the space time. It can be said that diffusion of lignin from the surface of the fibers occurred to some extent for spruce pulp at all levels of kappa number.

The correlations between the mean residence time and the space time for kraft spruce pulp with different levels of lignin content are shown in **Table IV** with correlation coefficient and the range of porosity shown in Table I under the experimental conditions. Porosity of the pulp beds were scattered and found no considerable dependence on the consistencies of the pulp beds in the experimental region.

The overall comparison of the dependence of mean residence time on the space time for the washing of the kraft spruce pulp cooked at different levels of kappa number is shown in **Fig. 6**. The differences in the individual level of kappa number were not substantial. Although the results were scattered, the increasing linear trend of the mean residence time with the space time was obvious. It might



6. Overall relationship of the mean residence time as a function of space time for kraft spruce pulp with various kappa numbers: (○) 18.1; (+) 19.6; (◇) 22.8; (×) 32.3; (⊙) 37.0; (□) 44.4; and (△) 50.1. Solid line: Eq. 10, and dashed line: $t_m = \tau$.

be postulated that the scattered results can be attributed by the geometrical difference of the bed formation. The dependence of the mean residence time on the space time of the spruce pulp washing derived for all data obtained for the kappa numbers from 18.1 to 50.1 can be expressed as follows:

$$t_m = 1.73 \tau \quad (10)$$

with a correlation coefficient, r , of 0.94. Potůček and Miklík [9] reported a correlation between the mean residence time and the space time for a hardwood pulp bed as follows:

$$t_m = 1.53 \tau \quad (11)$$

The variations of the correlation equations, Eq. 10 and

Kappa number	Before washing	18.1	19.6	22.8	32.3	37.0	44.4	50.1
	After washing	15.7	16.5	19.6	28.5	34.1	40.1	44.4
Lignin content	Before washing, %	3.74	3.89	4.52	5.65	6.39	7.33	8.47
	After washing, %	3.70	3.64	4.19	5.26	6.05	7.07	8.07

V. Kappa number and residual lignin content for the kraft spruce pulp before and after displacement washing.

Eq. 11, revealed that the geometric properties of the pulp beds must be different. Since the space time is proportional to the void space in the bed, however, leaching from the pulp surface must be taken into account. In our study, the porosity of the pulp bed was varied from 0.31 to 0.56 at a bed consistency ranging from 121 to 142 kg m⁻³ for the kraft spruce pulp, while the authors [9] reported a porosity range from 0.51 to 0.63 for kraft hardwood pulp. Lower values of porosity in kraft spruce pulp beds were in accordance with their permeability of 0.23×10^{-12} to 2.99×10^{-12} m², whereas in the case of hardwood pulp beds, the values were 0.9×10^{-12} to 2.8×10^{-12} m² [9]. Thus, for spruce pulp, the difference between the mean residence time of the lignin in the bed and the space time is greater than that for hardwood pulp, where a relatively larger part of the black liquor is located in the inter-fiber pores.

Residual lignin content

Chemical analysis of the kraft spruce pulps with seven different kappa numbers was performed to compare the effect of washing on the chemical composition. Kappa number is used to obtain information about the degree of delignification in chemical pulping. It indirectly expresses the amount of residual lignin present in the pulp [30]. The kappa number and residual lignin content were measured before and after displacement washing of the kraft spruce pulp to examine the displacement washing effect (**Table V**). Effective displacement washing should reduce the kappa number for some units [31]. In our study, the reduction of the kappa number of the spruce pulp was found after displacement washing. The maximum 5.7 units of kappa number depletion was recorded for the spruce pulp with the kappa number of 50.1, whereas the reduction was only 2.4 units for the pulp with the kappa number of 18.1.

The leaching of lignin from the inter-fiber and intra-fiber interstitial space during displacement washing resulted in the reduction of kappa number [25]. The displacement washing of kraft beech pulp with the kappa number varied from 14.1 to 51.6 showed 1 to 3 units of reduction in kappa number [18]. Ala-Kaila et al. [32] reported the reduction of the kappa number to 5.5 units for Scandinavian birch kraft pulp. It was assumed that the pulp with more residual lignin content facilitated more leaching of lignin during washing. As a result, variation of the kappa number reduction was observed with the kraft spruce pulps having various

levels of lignin content.

Because the kappa number decreased after displacement washing, it is assumed that the lignin content of washed pulp must be lower than that of the pulp before displacement washing. After the chemical analysis of the washed pulp, it was found that the reduction of lignin content was highest with the pulp having a kappa number of 50.1. The results strengthen the argument for higher leaching of lignin during displacement washing for the kraft spruce pulp. It was observed that the softwood with Klason lignin of 30.44% showed lower washing efficiency than the hardwood with Klason lignin of 24.47%. Generally, softwood contains higher lignin than hardwood. After pulping, softwood pulp suspensions contain higher lignin. Researchers [7,9] showed that the higher initial lignin content is one of the responsible factors for the lower washing efficiency of softwood pulp. Our results also strengthen the argument of lower efficiency of displacement washing for the spruce pulp with higher initial lignin content than the hardwood.

CONCLUSIONS

The displacement washing was justified using the stimulus response technique. The variations of the washing curve profile were negligible at the individual kappa number level. However, the washing curves of kraft spruce pulps were relaxed and absent from the plug flow in comparison with the short-fibered beech pulp. Although the wash yield and the Péclet number of the kraft spruce pulps were much lower than the beech pulp, the variation in the individual level of the kappa number was not noteworthy. The wash yield increased with increasing Péclet number like typical pulp washing, though the Péclet numbers were scattered in each level of kappa number. The dependence of wash yield and bed efficiency on the Péclet number and kappa number showed that the wash yield and bed efficiency increased not only with increasing Péclet number, but also with increasing kappa number.

Due to heterogeneity of the pulp bed, the time parameters were scattered over a longer time at the individual kappa number levels as compared to the beech pulp. Nevertheless, the linear dependence between both time parameters was obvious. In the correlation between mean residence time and space time, leaching of lignin might play an important role, along with the void volume in the pulp

bed. The residual lignin content in the spruce pulp was reduced in the displacement washing. The reduction of the residual lignin was proportional to the kappa number of the kraft spruce pulp. Overall, it was observed that the washing efficiency of the kraft spruce pulp mostly depends on the physical and geometrical properties of the pulp bed and is less dependent on the degree of delignification when the washing was carried out with the same type of pulp.

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LITERATURE CITED

1. Wilson, J., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1993, p. 155.
2. Grähs, L.E., *Sven. Papperstidn.* 79(3): 84(1976).
3. Grähs, L.E., *Sven. Papperstidn.* 79(4): 3(1976).
4. Lee, P.F., *Tappi* 62(9): 75(1979).
5. Poirier, N.A., Crotogino, R.H., and Douglas, W.J.M., *Can. J. Chem. Eng.* 66(6): 936(1988). <https://doi.org/10.1002/cjce.5450660607>.
6. Trinh, D.T., Poirier, N.A., Crotogino, R.H., et al., *J. Pulp Pap. Sci.* 15(1): 28(1989).
7. Potůček, F., *Collect. Czech. Chem. Commun.* 62(4): 626(1997). <https://doi.org/10.1135/cccc19970626>.
8. Potůček, F. and Marhanová, M., *Chem. Pap.* 54(4): 221(2000).
9. Potůček, F. and Miklík, J., *Chem. Pap.* 64(2): 147(2010). <https://doi.org/10.2478/s11696-009-0078-7>.
10. Potůček, F. and Hájková, K., *Chem. Pap.* 69(8): 1067(2015). <https://doi.org/10.1515/chempap-2015-0106>.
11. Lee, P.F., *Tappi J.* 67(11): 100(1984).
12. Hakamäki, H. and Kovasin, K., *Pulp Pap. Can.* 86(9): T243(1985).
13. Crotogino, R.H., Poirier, N.A., and Trinh, D.T., *Tappi J.* 70(6): 95(1987).
14. Smith, R.J. and Duffy, G.G., *Appita Annu. Gen. Conf. Proc.*, 53rd, 1999, p. 275.
15. Potůček, F., Rahman, M., and Miklík, J., *Cellul. Chem. Technol.* 54(9–10): 943(2020). <https://doi.org/10.35812/CelluloseChemTechnol.2020.54.91>.
16. Potůček, F. and Miklík, J., *Acta Fac. Xylo. Žvolen* 53(A): 49(2011).
17. Ingmanson, W.L., *Chem. Eng. Prog.* 49(11): 577(1953).
18. Miklík, J., "Displacement washing of hardwood pulp," Ph.D. thesis, University of Pardubice, Pardubice, Czech Republic, 2014.
19. Potůček, F. and Rahman, M.M., *Cellul. Chem. Technol.* 52(5–6): 393(2018).
20. Rainey, T.J., Doherty, W.O., Martinez, D.M., et al., *Appita J.* 62(4): 296(2009).
21. Lindsay, J.D., *Tappi J.* 77(6): 225(1994).
22. Poirier, N.A., Crotogino R.H., Trinh, D.T., et al., *Pulp Washing Symp.*, Finnish Pulp and Paper Research Institute, Espoo, Finland, 1987.

ABOUT THIS PAPER

Cite this article as:

Rahman, M. and F., Potůček *TAPPI J.* 20(9): 553(2021). <https://doi.org/10.32964/TJ20.9.553>

DOI: <https://doi.org/10.32964/TJ20.9.553>

ISSN: 0734-1415

Publisher: TAPPI Press

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Pulp washing is one of the crucial operations in the pulp industry. The influence of residual lignin on the washing efficiency has been studied in Ph.D. research. This research is a continuation of the previous published results on displacement washing of softwood and hardwood pulp, washing with water at different temperatures, and washing of kraft and sulfite pulp. The influence of the degree of delignification on the washing efficiency has not yet been published in a comprehensive form.

The most difficult aspect of this research was that the heterogeneity of pulp beds, in terms of the geometric configuration of the fibers, gives scattered results. It follows that precise experiments are required.

We discovered that the influence of residual lignin content on pulp washing efficiency was small. Also, it was interesting to find that

many parameters influence pulp washing. The results obtained here on a laboratory scale can be a guide for the design of countercurrent washing systems with improved efficiency. The next step is to calculate the number of ideal stages that characterize the efficiency of industrial washers.

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23. Levenspiel, O. and Smith, W.K., *Chem. Eng. Sci.* 6(4–5): 227(1957).
[https://doi.org/10.1016/0009-2509\(57\)85021-0](https://doi.org/10.1016/0009-2509(57)85021-0).
24. Levenspiel, O., *Chemical Reaction Engineering*, John Wiley & Sons, New York, 1962.
25. Potůček, F., *Pap. Celul.* 56(1): 8(2001).
26. Arora, S., Kaur, I., and Potůček, F., *Braz. J. Chem. Eng.* 32(2): 563(2015). <https://doi.org/10.1590/0104-6632.20150322s00003160>.
27. Van Der Laan, E.Th., *Chem. Eng. Sci.* 6: 187(1957).
28. Brenner, H., *Chem. Eng. Sci.* 17(4): 229(1962).
[https://doi.org/10.1016/0009-2509\(62\)85002-7](https://doi.org/10.1016/0009-2509(62)85002-7).
29. Cullinan, H.T., *Appita J.* 44(2): 91(1991). <https://doi.org/10.1063/1.2810051>.
30. Hatfield, R. and Fukushima, R.S., *Crop Sci.* 45(3): 832(2005).
<https://doi.org/10.2135/cropsci2004.0238>.
31. Potůček, F., *Cellul. Chem. Technol.* 37(1-2): 141(2003).
32. Ala-Kaila, K., Li, J., Sevastyanova, O., et al., *TAPPI J.* 2(10): 23(2003).