DISPLACEMENT WASHING OF KRAFT SPRUCE PULP COOKED TO LOW KAPPA NUMBER

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Abstract

The paper deals with the displacement washing of unbleached pulp cooked from spruce wood by kraft pulping process under laboratory conditions. Using the step function input change method, the washing breakthrough curves measured for alkali lignin as a tracer were described by the dispersed plug flow model, containing dimensionless criterion, the Péclet number. Besides the traditional wash yield, the relationship between the Péclet and Reynolds numbers was investigated as well. The results obtained for spruce pulp were compared with those for kraft beech pulp published earlier. The pulp yield achieved for spruce pulp was found to be lower than that for beech pulp.

Key words: displacement washing, kraft softwood pulp, wash yield, dispersed flow model

Introduction

The kraft pulping industry is the first known to combine pulp washing with the recovery of materials used and produced in the wood cooking process. The initial motivation behind materials recovery is the higher cost of chemicals used in the kraft process compared to those used in the sulphite process. For the kraft process to be economically viable, it is imperative that a very high amount of the cooking chemicals be recovered and reused[1].

Hence, brownstock washing is an important and critical step in processing lignocellulosic materials for making paper and related products. The imperative objective of brownstock washing is to remove cellulose fibres from the black liquor, which mainly include alkali, sodium salts, lignin, and other chemically degraded wood components, while using a minimal amount of wash water[2].

The digester discharged cooked pulp mixture consist of a pulp-liquor suspension containing two main phases: free liquor phase and fibre phase. The fibre phase includes wood fibres and the liquor entrained insides the fibres. The entrained liquor is in close contact with the fibres and can be assumed to behave as immobile liquor phase connected to the free liquor through mass transfer. The free liquor is quite easily removed during washing whereas the immobile liquor can only be removed by diffusion and capillary force[2].

Brownstock washing can be carried out in four basic processes known as dilution, dewatering, diffusion, and displacement[1]. Displacement washing process requires the lowest of amount of wash liquor among the four washing processes. The displacement washing is affected by many process variables: consistency of pulp bed, height of pulp bed, wash liquor velocity, temperature of wash liquor, variation of pulp, and heterogeneity of pulp bed. Because of complexity of the relationships between these process variables and the washing efficiency, as well as the use of different kinds of pulp and experimental techniques, the results so far reported disagree with each other[3].

Therefore, the present paper is aimed to investigate the displacement washing of unbleached pulp cooked to relatively low kappa number from spruce wood by the kraft pulping process.

Experimental

Wood chips were collected from the Mondi Pulp and Paper Mill. The composition of collected wood chips sample was heterogeneous which contain many undesirable particles such as oversized chips, bark, and knots. These unwanted particles were sorted out by hand to an almost unified chip composition in accordance with TAPPI Test Method T 265.

Before starting batch cooking experiments, the chips were stored in the laboratory. Kraft cooking experiments were carried out on a multiple bomb assembly consisting of six 0.75 L stainless steel bomb digesters of 90 g spruce wood capacity. Cooking conditions, which were held constant, were as follows: 18 % active alkali charge, 4:1 liquor to wood ratio, and 168 °C cooking temperature. Industrial white liquor at a sulfidity of 28 % was used.

The temperature regimes of cooking procedure were as follows: 45 min heating to 110 °C, 45 min dwelling at 110 °C, 60 min heating to 168 °C, and then dwelling at cooking temperature, depending on the desired H-factor of 3 190 h. As soon as the H-factor of the cooking was achieved, the bombs were brought out from the micro-digester as quickly as possible and cooled down under cold water to stop down further delignification. Then the pulp was disintegrated with laboratory disintegrator and washed up with tap water by dilution/thickening way, screened manually using 10-mesh sieve, and dewatered to consistency of approximately 30 %, using a laboratory centrifuge machine. The kappa number of spruce kraft pulp was determined according to TAPPI Test Method T 236 om-99.

The displacement washing was simulated under laboratory conditions. The stimulus-response experiments, using a step input, were performed in the displacement washing cell consisting of a vertical glass cylinder 110 mm high, having 35 mm inner diameter. The fibre bed occupied the volume between the permeable septum and piston. The experimental apparatus was similar to that used by Lee[4].

For each experiment, the slurry of unbeaten unbleached kraft pulp in black liquor was used. After compressing it to the desired thickness of 30 mm, the consistency, *i. e.*, mass concentration of moisture-free pulp fibres in the bed was maintained within the limits from 127.1 to 131.5 kg m^{-3}, the mean value being 128.2 kg m^{-3}. Using a Kajaani analyser, the length of softwood fibres in the wet state was characterized by the weighted average of 2.77 mm, as well as the numerical average of 1.91 mm. Estimated coarseness of fibres was about 0.103 mg m^{-1}. The degree of pulp delignification, expressed in terms of the kappa number, was found to be 18.1. The pulp beds were not mechanically conditioned and were used as prepared.

Concentration of alkali lignin in the black liquor taken from SuperBatch cooking plant was 61 g dm^{-3}. Further properties of sulphate liquor were as follows: solids content of 21.4 %, of which the ash made up 64 %, and organics 36 %, density of 1097 kg m^{-3} at 25 ^{o}C, and pH value of 12.0.

Distilled water at a temperature maintained at 25 ^{o}C was employed as wash liquid. The superficial wash liquid velocity, based on empty cross-sectional area, varied in the range from 0.05 to 0.2 mm s^{-1}. Samples of the washing effluent leaving the pulp bed were analysed for alkali lignin, using an ultraviolet spectrophotometer Cintra 10e operating at the wavelength of 295 nm. More detailed description of experiments can be found elsewhere[3]. Analogous measurements at various consistencies of the bed were focused on the determination of the effective specific volume and surface of pulp fibres according to Ingmanson[5].

Results and Discussion

Washing curves

A response to step change in concentration provided time dependences called washing or also breakthrough curves. In order to compare displacement washing process for various wash liquid velocity, the washing curves were plotted as the dependence of dimensionless concentration of a tracer, in our case alkali lignin, in the outlet stream expressed as ρ_e/ρ_0, against to the wash liquor ratio, RW, defined as the mass of wash liquid passed through the bed at that time divided by the mass of liquor originally present in the bed.

A typical breakthrough curve measured for spruce pulp is shown in Fig. 1. The first portions of the liquor discharged from the pulp bed are of the same concentration as the mother liquor. Then, the concentration of a solute in the outlet stream drops very rapidly. In this washing period, it can be supposed that the major part of the mother liquor in interparticle voids is removed and replaced by the wash liquid. At the end of the washing, the solute adsorbed on the surface of the fibres, as well as the solute inside the fibre walls is being transferred by diffusion to the wash liquid surrounding the fibres. In this last period, the leaching operation prevails over displacement mechanism.

For comparison, a breakthrough curve measured for displacement of black liquor from pulp bed formed from kraft beech pulp fibres cooked to the kappa number of 14.1 (ref.[6]) is also demonstrated in Fig. 1. Our results showed that both systems differ markedly from one another. From Fig. 1 follows that the breakthrough curves for spruce and beech pulp fibres approach that of plug flow. The flat profile of the breakthrough curve obtained for spruce pulp fibres having a kappa number of 18.1 is probably the result of the nature of pulp bed which can be characterised as an unmovable packing dumped randomly into the washing cell, along with black liquor occurring both in the void spaces and inside porous compressible particles. The ratio of the weighted to arithmetic average length, which is a measure of the polydispersity of fibre length, was roughly the same for the both pulps, 1.43 and 1.45, for hardwood and softwood fibres, respectively.

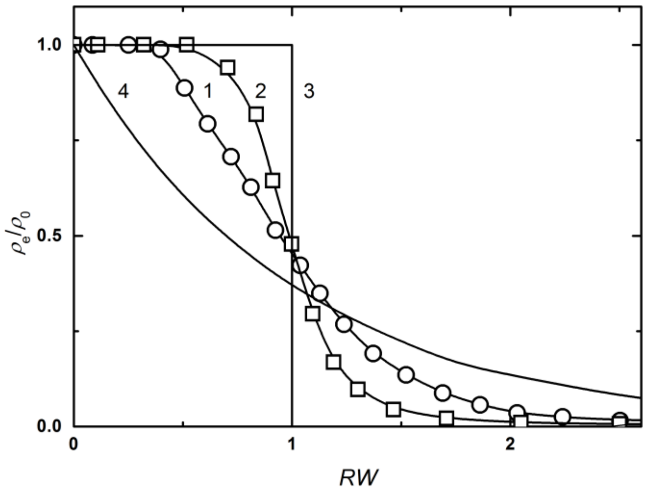

Figure 1. Typical displacement washing curves:
1 – spruce pulp (*Pe* = 10.2), 2 – beech pulp[6] (Pe = 42.9), 3 – plug flow, 4 – perfectly mixed flow

Péclet number – Reynolds number relationship

The shape of the washing curve can be characterised in terms of the dimensionless Péclet number, derived from the mass balance of the tracer for a given system in unsteady state, in the following form

$$Pe = \frac{h\,u}{D\,\varepsilon} \quad . \tag{1}$$

The determination of the Péclet number from the residence time distribution measured for displacement washing can be found in the previous paper[3]. The Péclet number obtained on the basis of breakthrough curve characterises not only the degree of backmixing of fluid flowing through a packed bed, but also, particularly, the ratio of the bulk mass flow to the dispersion mass flow. In accordance with the shape of washing curves, the Péclet number evaluated for spruce pulp beds varied in the limits of 10 to 20, while the values of the Péclet number obtained for beech pulp beds were in the range of 25 to 41 (ref.[6]). Presumably, the lower values of the Péclet number measured for pulp fibre bed represent more bridgings between particles and greater variations in local voidage which promote a channelling phenomenon. Of course, because of fibre swelling the mass transfer from within the fibre walls to the wash liquid must be taken into account.

The type of flow in a pore of given geometry may be characterized by the Reynolds number. For wash liquid flowing through an individual pore in a packed bed, the Reynolds number can be written in the form

$$Re = \frac{d_m u\,\rho}{\varepsilon\,\mu} \tag{2}$$

where $d_m = 4\,\varepsilon/(a_v\,(1\text{-}\varepsilon))$ is the hydraulic mean diameter defined as four times the cross-sectional area divided by the wetted perimeter of the pore.

The average porosity of pulp bed was evaluated on the basis of permeability determined experimentally. Depending on the consistency of pulp bed, the permeability varied within the limits of 1.2×10^{-12} to 3.0×10^{-12} m^2. For comparison, the permeability of the bed of glass beads was found to be 9×10^{-11} m^2. More details can be found in the previous paper[7].

In Fig. 2, the Péclet number is plotted as a function of the Reynolds number. From Fig. 2 it seems that the Péclet number is independent upon the Reynolds number ranging from 2.73×10^{-3} to 1.04×10^{-3}. The Péclet number varied within the 95 % confidence limits from 13.1 to 16.1, with an average value of 14.6. The values of the Reynolds number indicate that the assumption of the laminar character of wash liquid motion was fulfilled. Owing to low number of measurements, it is necessary to verify the relationship between the Péclet number and Reynolds number on other pulp fibres for greater interval of the wash liquid velocity.

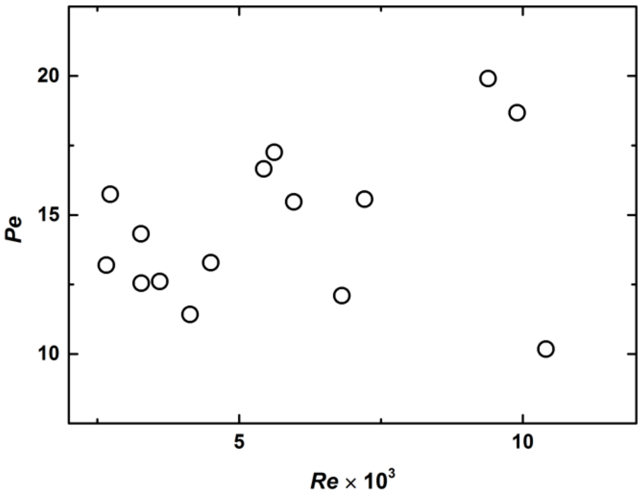

Figure 2. Péclet number as a function of Reynolds number for kraft spruce pulp fibre bed

Our results can be compared with those obtained by the other authors. Miller and King[8] who investigated axial dispersion in laminar flow through beds of 0.051, 0.099, and 0.47 mm microspheres, and 1.4 mm glass spheres in the range of Reynolds numbers between 0.003 and 40 found that the dependence of the Péclet number on the Reynolds number at first drops, passes through a minimum near $Re \approx 10$, and then rises. For glass spheres, Raschig rings, Berl saddles, and Intalox saddles as packing, Ebach and White[9] found that the Péclet number varied from 0.3 to 0.8 for the range of Reynolds numbers from 0.01 to 150. On the other hand, using the frequency response technique, Strang and Geankoplis[10] report that the Péclet number is approximately constant at a value of 0.88 over the range of Reynolds numbers of 12 to 42 for the glass beads which had an average diameter of 6 mm. Montillet *et al.*[11] characterized the hydrodynamic behaviour of a liquid flowing through various nickel foams, as well as packed beds and proposed a single correlation in the form $Pe = 0.43 \pm 0.10$ in the range $0.1 < Re < 100$ for fixed beds packed with cylinders, spheres, and nickel foams. Using pulse and step response techniques, Leitao *et al.*[12] report a systematic study of liquid phase axial dispersion in columns packed randomly with granular sand. For the Reynolds number in the range from 1 to 50, the authors[12] derived the correlation between the Péclet and Reynolds number in the form $Pe = 0.508\ Re^{0.02}$. It should be stressed that the authors[8-10, 12], in contrast to our work, considered the Péclet number and Reynolds number based on the particle diameter, while the authors[11] used these dimensionless numbers based on the mean pore diameter.

Wash yield

The displacement washing curve area (Fig. 1) is directly proportional to the amount of alkali lignin removed from the bed. It must be emphasised that the washing experiments were finished at the wash liquor ratio equal to about 7 when the lignin concentration in the exit stream was lower than one thousandth of the initial lignin concentration in the pulp fibre bed.

Quality of the displacement washing can be characterised by the wash yield. The traditional displacement wash yield, $WY_{\mathrm{RW=1}}$, is defined as the amount of solute washed out at the wash liquor ratio equal to unity divided by the total amount of solute present in the bed at time equal to zero. This yield may be expressed as

$$WY_{\mathrm{RW=1}} = \frac{\int_{\mathrm{RW=0}}^{\mathrm{RW=1}} \frac{\rho_e}{\rho_0} \mathrm{d}(RW)}{\int_{\mathrm{RW=0}}^{\mathrm{RW\to\infty}} \frac{\rho_e}{\rho_0} \mathrm{d}(RW)} \quad . \tag{3}$$

The influence of the Péclet number on the wash yield is shown in Fig. 3. In spite of the scatter in the data, in the case of beech pulp fibres covering a range of the Péclet number from 25 to 41, it is evident that the wash yield slightly increases with increasing Péclet number for both softwood and hardwood pulps. The experimental points are located below the curve derived for the packed bed of non-porous particles by Brenner[13]. In contrast to the packed bed of non-porous particles[7], when the washing process is reduced to the displacement mechanism and interfacial mixing between the displaced and displacing fluids, leaching may play a significant role in the case of compressible porous fibres in the swollen state.

Comparing the spruce and beech pulp fibres, the greater values of the wash yield were achieved for beech pulp. Presumably, lower values of the Péclet number covering the range from 10 to 20 measured for softwood spruce pulp fibre bed can be ascribed to fingering or channelling phenomena typical for packed beds randomly formed from heterogenous particles.

Moreover, the high Klason lignin content of 30.4 mass % found in spruce is comparable with that of pine (29.5 mass %), while beech evidences the lower lignin content of 24.5 mass % (ref.[6]). Besides the degree of delignification, the initial alkali lignin concentration of the black liquor is affected by the lignin content in the wood samples. Lower values of the wash yield reported for spruce pulp can be also attributed to the high initial alkali lignin concentration of 61 kg m^{-3} in contrast to 27 kg m^{-3} in the case of beech pulp in the previous paper[6]. It was confirmed that hardwoods having generally lower lignin content, which is advantageous for delignification and following washing process, produce kraft pulps with better washability for lower alkali lignin concentration in the mother liquor is usually achieved. As previously reported (ref.[3]), the displacement wash yield decreases with increasing initial lignin concentration in the mother liquor. As for the values of the wash yield obtained in our work for the initial lignin concentration of 61 kg m^{-3}, Trinh *et al.*[14] reported the wash yield varying from 0.84 to 0.87 for initial lignin concentration of 25 kg m^{-3} in the bed of softwood pulp fibres.

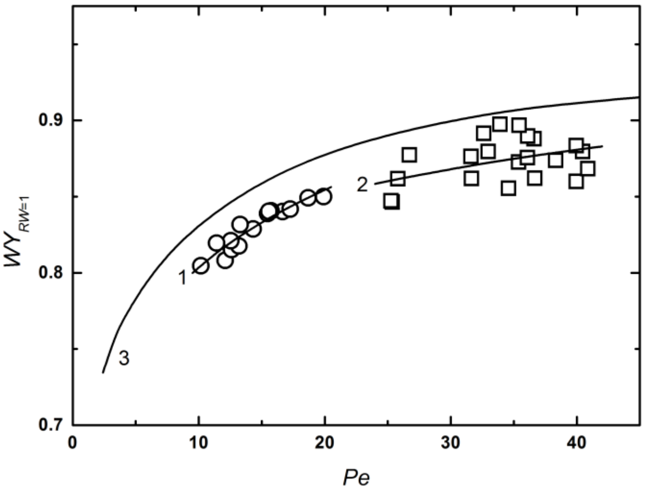

Figure 3. Displacement wash yield as a function of the Péclet number:
○ spruce pulp, □ beech pulp[6], 1 – Eq. (4), 2 – Eq. (5), 3 – according to Brenner[13]

On the basis of our own data measured for beech pulp bed, the effect of the Péclet number on the wash yield can also be expressed by the following correlation equation

$$WY_{\mathrm{RW}=1} = 0.656\, Pe^{0.0885} \tag{4}$$

with a mean relative quadratic deviation equal to 0.6 %. Since the values of regression coefficients, which were evaluated by the least square method, represent an estimate of the real values, the 95% confidence intervals were calculated as well. They are (0.647; 0.664) and (0.0837; 0.0932) for the coefficient and the power of the Péclet number, respectively. For the qualitative evaluation of the effect of the Péclet number on the wash yield, the following correlation equation

$$WY_{\mathrm{RW}=1} = 0.732\, Pe^{0.0503} \tag{5}$$

was developed for beech pulp beds in our previous work[6] with the mean relative deviation of 1.4 %.

Conclusions

The preliminary results obtained for spruce kraft pulp with the kappa number of 18.1 enabled that some conclusions valid within the framework of our study can be made.

(i) The displacement washing of softwood spruce pulp fibres is characterised by greater values of the Péclet number in comparison with hardwood beech pulp with kappa number of 14.1.

(ii) The Péclet number based on the pulp bed thickness seems to be independent upon the Reynolds number ranging within the limits of 2.73×10^{-3} to 1.04×10^{-3}.

(iii) The efficiency of the displacement washing increases with increasing the Péclet number. The wash yield for kraft spruce pulp was found to be lower in comparison with that published for beech pulp in our preceding papers.

Acknowledgements

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Symbols

a_v	specific surface of pulp fibres, m^{-1}
D	axial dispersion coefficient, m^2 s^{-1}
d_m	hydraulic mean diameter (= $4\ \varepsilon/(a_v\ (1-\varepsilon))$), m
h	thickness of bed, m
Pe	Péclet number based on bed thickness defined by Eq. (1), dimensionless
Re	Reynolds number (= $4\ u\ \rho/(a_v\ \mu\ (1-\varepsilon))$), dimensionless
RW	wash liquor ratio, dimensionless
u	wash liquid superficial velocity, m s^{-1}
$WY_{RW=1}$	wash yield at RW = 1 defined by Eq. (3), dimensionless

Greek letters

ε	average porosity of packed bed, dimensionless
μ	wash liquid viscosity, Pa s
ρ	wash liquid density, kg m^{-3}
ρ_e	exit solute (in our case alkali lignin) concentration from bed, kg m^{-3}
ρ_0	initial solute (in our case alkali lignin) concentration in bed at $t = 0$, kg m^{-3}

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