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WASHING OF SODA PULP COOKED FROM RAPESEED STRAW

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ABSTRACT

The aim of this work was to investigate the displacement washing process of soda pulp cooked from rapeseed straw from the point of view of chemical-engineering analysis. Displacement washing process was described by displacement washing curves recorded for alkali lignin like a tracer. The shape of the washing curves obtained experimentally indicated that the displacement of black liquor was non-ideal, *i.e.*, it was between the ideal limits of plug flow and perfectly mixed flow. Mathematical treatment of the washing curves, which were obtained as a response to the step input signal, gave the dimensionless number known as the Péclet number characterizing the displacement of lignin from the pulp pad. For detailed description of displacement washing process, further parameters, such as the traditional wash yield, as well as axial dispersion coefficient, were also evaluated.

The preliminary results obtained showed that, similarly as for kraft softwood and hardwood fibres, the wash yield determined for soda rapeseed pulp was found to be lower than that for non-porous incompressible particles. Comparing our results for soda pulp with those reported for softwood and hardwood pulps earlier, the displacement front becomes irregular owing to the heterogeneity of soda pulp fibre bed having much greater hydraulic resistance. With respect to this fact, the greater scatter of the longitudinal dispersion coefficient was achieved for soda pulp fibres.

Key words: displacement washing; soda rapeseed pulp; wash yield; Péclet number; dispersion coefficient.

INTRODUCTION

Rapeseed, the third most important oilseed crop after soybean and palm, has been cultivated to produce seeds for oil and biodiesel production. The world wide planted area for rapeseed increases continuously. After harvesting, the amount of rapeseed straw remaining in the field is of 2.8 to 4.5 $t \cdot ha^{-1}$ (PETŘÍKOVÁ 1999). Recently, several authors (ENAYATI *et al*. 2009; MOUSAVI *et al*. 2013; POTŮČEK, MILICHOVSKÝ 2011; POTŮČEK *et al*. 2014) reported soda pulping of rapeseed straw and their results obtained in the laboratory scale showed that rapeseed straw can be considered as one of the basic resources of non-woody materials to pulp and paper production. Chemical composition and morphological properties along with pulping procedures of non-woody plants were reported in the review article (GURUNG, POTŮČEK 2013), including also strength properties of non-woody pulp fibres.

The objective of washing is to separate cellulose fibres from black liquor while using a minimal amount of wash water. Very often, pulp washing is a compromise between the cleanness of the pulp and the amount of wash water to be used. Pulp washing can be carried out by dilution/drainage or by displacement of the liquor, and most of the industrial washers combine both principles. A substantial amount of filtrate is trapped inside the fibre walls and between the fibre bundles, and is therefore not relevant to the drainage process. Displacement washing is based on the idea of replacing the liquor in the pulp web with wash liquor rather than mixing these two liquors (KROTSCHECK 2006). Appropriate displacement washing is of primary importance in obtaining good washing efficiencies with all types of washing equipment.

Although pulp washing together with cooking rank among the key unit operations in pulp manufacture, no research work concerning washing of rapeseed pulp was found in the literature. Therefore, the objective of this study was to conduct displacement washing of soda pulp cooked from rapeseed straw.

EXPERIMENTAL PART

Rapeseed straw (*Brassica napus* L. convar. *napus*, in our case winter hybrid genotype Rohan) collected from the field in Bohemian-Moravian Highlands was used for the pulping process. Raw materials consisted mainly of stalks, but approximately one third of total mass were valves of siliques.

The degree of delignification of pulp cooked by the batch soda process expressed by the kappa number was of 33.9. Using the Kajaani FS-100 instrument, the distribution of the fibre length was also measured for pulp cooked from rapeseed straw. The length of fibres in the wet state was characterized by the weighted average of 0.82 mm, as well as the numerical average of 0.36 mm.

Displacement washing experiments simulated under the laboratory conditions were performed in a cylindrical glass cell with inside diameter of 35 mm under constant pulp bed height of 30 mm. The fibre pulp bed occupied the volume between the permeable septum and a piston, covered with 45 mesh screens to prevent fibre loss from the bed.

Pulp beds were formed from a dilute suspension of unbeaten unbleached soda pulp in black liquor. Properties of black liquor were as follows: solids content of 11.3 % (of which ash presented 56 % and organic substances 44 %), density of 1061 $kg \cdot m^{-3}$ at 22 °C, pH value of 9.2, and alkali lignin concentration 27 $g \cdot dm^{-3}$. After compressing to desire thickness of 30 mm, the consistency, *i. e.*, mass concentration of moisture-free pulp fibres in the bed varied within the limits from 68 to 88 $kg \cdot m^{-3}$. The pulp beds were not mechanically conditioned and were used as formed.

To investigate the displacement washing process, the stimulus-response method was chosen. Distilled water at the temperature of 22 °C employed as wash liquid was distributed uniformly through the piston to the top of bed at the start of the washing experiment, approximating a step change in alkali lignin concentration. At the same time the displaced liquor was collected at atmospheric pressure from the bottom of the bed through the septum. The washing effluent was sampled at different time intervals until the effluent was colourless. Samples of the washing effluent leaving the pulp bed were analysed for alkali lignin using an ultraviolet spectrophotometer operating at a wavelength of 280 nm. Displacement washing experiments with pulp fibres including washing equipment were described in detail in the preceding paper (POTŮČEK 1997).

After completing the washing run, the volumetric flow rate of wash liquid was measured gravimetrically at the pressure drop of 7 kPa to determine a permeability and average porosity of the pulp bed. Analogous measurements at various consistencies of the bed were focused on the determination of the effective specific surface of pulp fibres according to INGMANSON (1953). The effective specific surface of soda pulp fibres was found to be 1.07 $m^2 \cdot g^{-1}$. For comparison, lower values of 0.988 $m^2 \cdot g^{-1}$ and 0.793 $m^2 \cdot g^{-1}$ were measured for short hardwood fibres (POTŮČEK, MIKLÍK 2010) and longer softwood fibres (POTŮČEK, PULCER 2004), respectively.

RESULTS AND DISCUSSION

For a better and more detailed description of the washing operation, a microscopic model has to be used. The dispersed plug flow model (LEVENSPIEL 1962) can be chosen to characterize the displacement of the black liquor from the pulp fibre bed. The response to the step input signal can be recorded as a time dependence of the solute (*e. g.*, alkali lignin) concentration in the output stream of effluent. Breakthrough curves obtained experimentally were normalized by plotting them on coordinates of the ratio of the instantaneous outlet to the initial mother liquor concentration in the bed *versus* the wash liquor ratio defined as the ratio of the mass of the wash liquor passed through the bed and the mass of the mother liquor present in the packed bed. A typical example of washing curves measured for alkali lignin is illustrated in Fig. 1, which shows also the logical limits of plug flow without diffusion and of infinite diffusion as with a fully stirred vessel.

Intrinsic properties of effluent stream leaving the bed are changed during displacement process. In Fig. 1, the density, ρ, viscosity, μ, and surface tension, σ, measured at a temperature of 22 °C for the black liquor (BL) and wash liquid (WL) are mentioned. At the beginning of a displacement, the first portions discharged from the bed are fully as concentrated as was the mother liquor. As soon as the first portion of wash liquid passes through the bed, the concentration of lignin drops very rapidly. The major part of mother liquor in interparticle voids is removed and replaced by wash liquid. In the last period, only remains of black liquor are removed from inside narrow pores and fibre walls. In contrast to the first two periods, in which the displacement operation is a dominant one, the leaching referring to the desorption and diffusion of solute from within the fibres prevails. The shape of washing curve including its tail is strongly influenced by a highly complex network of pores and by leaching of solute from within fibre walls into the wash liquid. It is necessary to note that the shorter time contact between the wash liquid and fibres the longer the tail on the washing curve can be achieved. Under our laboratory conditions, the average interstitial velocity of the wash liquid in the bed was quite low in the range from 0.1 to 0.4 $mm \cdot s^{-1}$. Then, the wash liquid was in contact with the fibres for a relatively long time. Owing to a tortuosity of pores, the wash liquid is forced to take a longer path than the bed thickness is.

The area below breakthrough curve expressed as the dependence of the dimensionless concentration of solute upon the wash liquor ratio, RW, is directly proportional to the amount of a solute removed from the pulp bed. Then, the quality of the displacement washing process can be characterized by the wash yield, $WY_{\mathrm{RW}=1}$, evaluated at the wash liquor ratio equal to unity as follows

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

A measure of lignin dispersion in the bed is indicated by the dimensionless Péclet number defined as

$$Pe = \frac{h\,u}{D\,\varepsilon} \tag{2}$$

This dimensionless parameter based on the height of the bed also signifies a ratio of the convective to the diffusive transport mechanisms. Details of the evaluation of the Péclet number can be found elsewhere (POTŮČEK 1997).

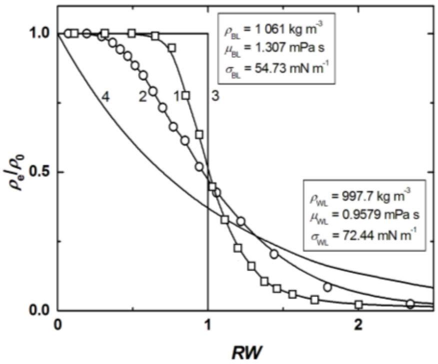

Fig. 1 Typical breakthrough washing curves: *Pe* = 41.1 (line 1), *Pe* = 6.1 (line 2), plug flow (line 3), perfectly mixed flow (line 4).

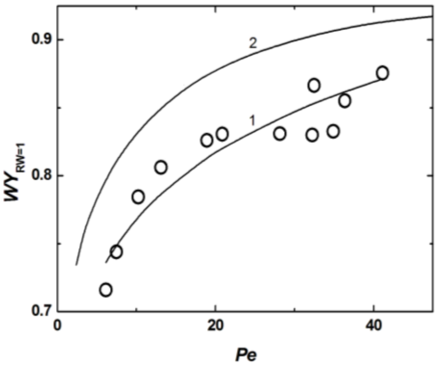

Fig. 2 Displacement wash yield as a function of the Péclet number (○). Equation (3) (line 1), non-porous particles according to BRENNER (1962) (line 2).

Wash yield data are illustrated as a function of the Péclet number in Fig. 2. The experimental points measured for pulp fibres are located below the curve which was derived for the packed bed of non-porous particles by BRENNER (1962). In contrast to the packed bed of non-porous particles, when the washing process is reduced to the displacement mechanism and interfacial mixing between the displaced and displacing fluid, the leaching can play a significant role in the case of compressible porous fibres in the swollen state.

For the data illustrated in Fig. 2, the influence of the Péclet number on the wash yield can be correlated by the following equation

$$WY_{RW=1} = 0.63\,Pe^{0,087} \tag{3}$$

valid in the range of the Péclet number of 6 to 41. The equation (3) fitted the data with a mean relative quadratic deviation, δ (defined in Symbols) of 1.9 %. 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 also calculated. They are for the coefficient 0.63 ± 0.012, and for the power of the Péclet number 0.087 ± 0.0063.

This correlation confirmed again that the wash yield depends upon the Péclet number in a small degree. The dependence between the Péclet number and the wash yield is in good agreement with that obtained earlier for kraft softwood pulp (POTŮČEK 1997; POTŮČEK, MARHANOVÁ 2000; POTŮČEK, PULCER 2004) and kraft hardwood pulp (POTŮČEK, MIKLÍK 2010) expressed by the correlation equations as $WY_{RW=1} = 0.73\,Pe^{0.039}$, and $WY_{RW=1} = 0.70\,Pe^{0.065}$, respectively.

In practice, the heterogeneity of the fibre mat could create channelling or dead zones. This feature leads to a deviation from ideal plug flow and a decrease in washing efficiency. In displacing a fluid from a porous medium, the displacement front will became irregular, with channels, or fingers, of the injected fluid penetrating and bypassing the resident fluid.

As follows from Eq. (2), the Péclet number comprises the dispersion coefficient, which is analogous to and has the same units as the diffusion coefficient. According to

SHERMAN (1964), the dispersion coefficient in beds of granular and synthetic fibrous media is of the order of 10^{-6} $m^2 \cdot s^{-1}$ for the displacement velocities normally encountered in practice. Of course, if miscible fluids are flowing through the porous medium, dispersion may be greater than that due to diffusion alone. One cause of fluid dispersion is the fact that under the same pressure gradient, fluid in large pores will travel more rapidly than fluid particles in small pores. Pore size distribution or wall effects are parameters inducing the anomalous dispersion, particularly in consolidated porous media, by the fluctuations of the local velocity caused by the particle configuration.

The axial dispersion coefficient calculated for soda pulp fibre bed was much more scattered and the values of axial dispersion coefficient were greater than those for glass rings (Fig. 3). These results showed that the bed formation is a critical step. Comparing to packed beds from non-porous, incompressible particles such as glass spheres or rings, fibre beds need to be formed again for each series of measurements. Even if the experimental conditions are strictly identical, it is obviously difficult to form the same bed (MAURET, RENAUD 2002). As a consequence, the scattering of fibre pulp data is high. Moreover, the way of bed formation can caused fluid channelling in the bed. It is worth mentioning that a linear dependence of the axial dispersion coefficient on the wash liquid superficial velocity was found for both hardwood fibres (POTŮČEK, MIKLÍK 2010) and softwood fibres (POTŮČEK, PULCER 2004) .

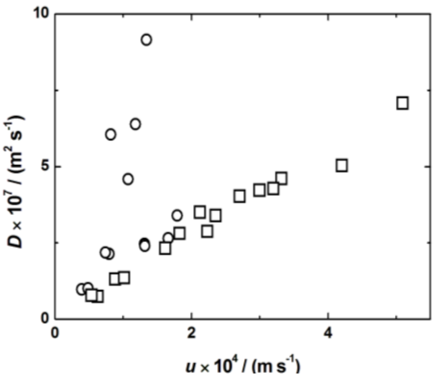

Fig. 3 Influence of the wash liquid superficial velocity on the axial dispersion coefficient for pulp fibres (○), glass rings (POTŮČEK, PULCER 2004) (□)

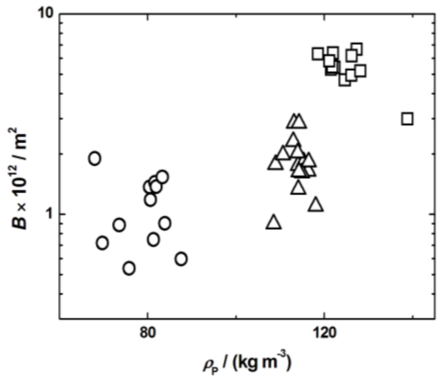

Fig. 4 Pulp bed permeability as a function of bed consistency for soda pulp (○), for kraft hardwood pulp (POTŮČEK, MIKLÍK 2010) (△), for kraft softwood pulp (POTŮČEK, PULCER 2004) (□)

With respect to the channelling of the displacing liquid through a more viscous solute-rich liquor, the mobility of the displacing fluid (defined as the ratio of the permeability to viscosity) is more significant than straight viscosity. When the mobility of the displacing fluid is less than the mobility of the displaced liquid, the tendency for channelling is suppressed (POTŮČEK 2003). Also, in our preceding work (POTŮČEK, MARHANOVÁ 2000), lower mobility of non-ionic polyacrylamide solutions in comparison with water had a favourable effect on displacement washing efficiency.

It is worth mentioning that the soda pulp bed formed from rapeseed fibres has greater hydraulic resistance in comparison with beds of softwood and hardwood fibres. Assuming that Darcy´s law holds, the permeability may be determined. The Reynolds number, *Re*, (defined in Symbols) ranging of 1.03×10^{-3} to 4.79×10^{-3} confirm streamline flow of wash liquids flowing through pulp fibre bed. Figure 4 portrays the permeability measured for pulp beds from rapeseed, hardwood, and softwood fibres. It is evident that the soda pulp cooked from rapeseed straw has lower permeability than softwood and hardwood pulps. Thus, pulp fibre beds tested in our work may be characterized like compressible unmovable beds, yet each of them is different with respect to local porosity, as well as space orientation of the fibres within a bed.

CONCLUSIONS

The results obtained showed that the pith of non-wood plants composed mainly of parenchyma cells and vessel elements can cause serious problems, such as washing and drainage problems in papermaking.

The hydraulic resistance of the soda pulp fibres cooked from rapeseed straw to the delignification degree expressed by the kappa number of 33.9 was much greater than that for kraft softwood or hardwood pulp fibres. The beds of soda pulp fibres presented much greater values of the longitudinal dispersion coefficient in comparison with non-porous particles. The displacement wash yield for soda pulp fibres showed an increasing trend with increasing the Péclet number in agreement with the results obtained for softwood and hardwood fibres in our previous papers.

SYMBOLS

B	permeability, m^2
D	axial dispersion coefficient, $m^2 \cdot s^{-1}$
h	height of bed, m
n	number of measurements
Pe	Péclet number based on bed height defined by Eq. (2)
Re	Reynolds number based on hydraulic diameter of pore (= $4\, u\, \rho_{WL} / (a_v\, (1-\varepsilon)\, \mu)$)
RW	wash liquor ratio
u	superficial wash liquid velocity, $m \cdot s^{-1}$
$WY_{RW=1}$	wash yield at $RW = 1$ defined by Eq. (1)

Greek letters

δ	mean relative quadratic deviation of wash yield defined as

$$\delta = \left[\frac{1}{n} \sum_{i=1}^{i=n} \left(\frac{WY_{\exp} - WY_{calc}}{WY_{\exp}} \right)_i^2 \right]^{1/2} \times 100, \%$$

ε	average effective bed porosity
μ	dynamic viscosity, Pa·s
ρ_e	exit lignin concentration from bed, $kg \cdot m^{-3}$
ρ_P	consistency (mass concentration) of pulp bed, $kg \cdot m^{-3}$
ρ_0	initial lignin concentration in bed, $kg \cdot m^{-3}$
σ	surface tension, $N \cdot m^{-1}$

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