DISPLACEMENT WASHING OF SODA PULP COOKED FROM RAPESEED STRAW WITH AND WITHOUT SILIQUE VALVES

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The paper deals with the displacement washing of unbleached pulp cooked from rapeseed straw by the soda 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. The preliminary results obtained for soda rapeseed pulp were compared with those for kraft hardwood pulp published earlier. The pulp yield measured for soda pulp was found to be lower than that for hardwood pulp which manifested lower hydraulic resistance. The presence of silique valves in rapeseed straw has a considerable impact on the exit concentration profile of alkali lignin displaced from the pulp fibre bed.

Key words: displacement washing, soda rapeseed pulp, wash yield, Péclet number

Introduction

Non-wood raw materials including agricultural residues and annual plants could be effective source to produce pulp and paper with acceptable properties, especially in countries with insufficient forest resources[1]. Compared to wood, non-wood raw materials are similar in cellulose, lower in lignin and higher in pentosans (hemicelluloses) and silica content.

Rapeseed along with soybean and palm ranks among the three most important oilseed crops in the world and it is mainly used for vegetable oils and biodiesel production at present. The world wide planted area for rapeseed increases continuously. Recently, several authors[2–5] have 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 sources of non-wood materials for pulp and paper production.

Although pulp washing together with cooking belong to the key unit operations in pulp manufacture, no research work concerning washing of rapeseed pulp was found in literature. The purpose of pulp washing is to remove the spent pulping liquor from the pulp leaving the cooking process. Owing to evaporation of wash liquors leaving the washing system before their recovery, the washing process must compromise between the cleanliness of the pulp and the amount of water to be used.

Therefore, the present paper is aimed to investigate the displacement washing of unbleached soda pulp made from rapeseed straw with and without silique valves by the batch soda pulping process.

Experimental

Rapeseed straw (*Brassica napus* L. convar. *napus*, in our case winter hybrid genotype PR45DO3) collected from the field in Polabian lowlands near the city of Pardubice was used in the pulping process. Raw materials consisted mainly of stalks, but approximately one third of total mass were valves of siliques.

Prior to the cooking experiments, rapeseed straw was cut into 2–3 cm length chips. Batch soda pulping of rapeseed straw was carried out in a laboratory rotary digester comprising six autoclaves of 750 cm^3 capacity, immersed in an oil bath. The cooking conditions, when the rejects amount was acceptable, were selected as follows: liquor-to-raw material ratio of 5:1, alkali charge of 19 mass % expressed as Na_2O per oven-dried raw material, and cooking temperature of 160 ºC. The temperature regime was as follows: 45 min heating to 105 °C, 30 min dwelling at 105 °C, 30 min heating to 160 °C, and then dwelling at the cooking temperature. The batch cooking was ended as soon as the H-factor reached the value of 2,205 h. The corresponding cooking time at the cooking temperature was 185 min. More details on the batch cooking of rapeseed straw can be found in our previous paper[5].

The degree of delignification expressed by the kappa number was 43.8 and 39.4 for pulp cooked from a blend of stalks and silique valves and for pulp cooked from stalks only, respectively. Using a Kajaani FS-100 instrument, distribution of the fibre length was also measured for pulp cooked form rapeseed straw.
Displacement washing experiments simulated under laboratory conditions were performed in a cylindrical glass cell with the 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 mass % (of which ash presented 53 % and organic substances 47 %), density of 1060 kg m^{-3} at 22 °C, pH value of 9.2, and alkali lignin concentration of 28 g dm^{-3}. After compression to the desired thickness of 30 mm, the consistency, *i. e.*, mass concentration of moisture-free pulp fibres in the bed varied within the limits from 76 to 92 kg m^{-3}. The pulp beds were not mechanically conditioned and were used as prepared.
To investigate the displacement washing process, the stimulus-response method[6] was chosen. Distilled water at the temperature of 22 °C employed as wash liquid was distributed uniformly through the piston to the top of the bed at the start of the washing experiment, approximating a step change in the alkali lignin concentration. At the same time the displaced liquor was collected at the 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 Cintra 10e operating at the wavelength of 280 nm. Displacement washing experiments with pulp fibres including washing equipment were described in detail in the preceding paper[7].
After completing the washing run, the volumetric flow rate of the wash liquid was measured gravimetrically at the pressure drop of 7 kPa to determine the 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 volume and surface of pulp fibres according to Ingmanson[8].

Results and Discussion

Fibre characteristics

Fibre characteristics of soda pulps cooked from rapeseed straw are compared with those for kraft pulp from a blend of hardwoods, namely beech 55 %, oak 16 %, Turkey oak 8 %, acacia 4 %, hornbeam 5 %, poplar 6 %, and other 6 % (ref.[9]) in Table I. Pulp fibres manufactured from rapeseed straw are short, with an average length less than 1 mm. The presence of silique valves in straw resulted in greater polydispersity in the fibre length in comparison with the soda pulp cooked from stalks only. For comparison Enayati *et al.*[2] and Mousavi *et al.*[3] reported the fibre length of 1.17 mm for pulp from canola stalks and of 1.03 mm for pulp from rapeseed straw, respectively.

Table I
Fibre characteristics of pulp cooked from rapeseed straw and a blend of hardwoods[9]

Raw material	Kappa number	Weighted average length, mm	Arithmetic average length, mm	Effective specific volume cm^3 g^{-1}	Effective specific surface m^2 g^{-1}
Stalks with silique valves	43.8	1.01	0.40	4.57	1.502
Stalks only	39.4	0.81	0.74	5.22	1.425
Hardwoods	29.9	0.90	0.75	2.92	0.988

Breakthrough curves

The response to a step change in concentration provided time dependences called washing or also breakthrough curves. To compare the displacement washing process for various wash liquid velocity, the washing curves were plotted as the dependence of the dimensionless concentration of alkali lignin in the outlet stream expressed as ρ_e/ρ_0, against the dimensionless time, Θ, defined for the pulp fibre bed as

$$\Theta = \frac{t}{t_{\mathrm{m}}} \tag{1}$$

where the mean residence time, t_{m}, is given as

$$t_{\mathrm{m}} = \int_{t=0}^{t\to\infty} \frac{\rho_{\mathrm{e}}}{\rho_0}\,\mathrm{d}t \tag{2}$$

where t is the time of the start of experiment, and ρ_{e} and ρ_0 are the exit and initial alkali lignin concentration, respectively.

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

$$Pe = \frac{hu}{D\varepsilon} \tag{3}$$

where h is the thickness of the pulp bed, u is the wash liquid superficial velocity, D is the longitudinal dispersion coefficient, and ε is the average porosity of packed bed. Evaluation of the Péclet number from the breakthrough curves is described in detail in the previous paper[7].

Typical breakthrough curves measured for soda pulp cooked from rapeseed straw comprising stalks and silique valves are shown in Fig. 1. From the dimensionless concentration profile of alkali lignin in the exit stream (breakthrough curve 1 in Fig. 1), it is obvious that at first the mother liquor is displaced from the pulp bed. As soon as the first portion of the wash liquid passes through the pulp bed, the alkali lignin concentration in the exit stream drops very rapidly. At the end of the washing run, when the leaching of alkali lignin from fibre walls prevails over the displacement, a small tailing of the breakthrough curve can be observed.

It is worth mentioning that the formation of a pulp bed in a washing cell significantly influences the shape of the breakthrough curves. For comparison, breakthrough curve 2 approaching that of perfectly mixed flow is shown in Fig. 1. In contrast to pulp cooked from stalks only, for which the Péclet number varied within the range of 2.6 to 11.6, the Péclet number range of 3.1 to 42.5 was found for pulp cooked from a blend of stalks and silique valves. This fact can be probably attributed to the different polydispersity coefficient defined as a ratio of the weighted average length and the arithmetic average length of fibres in pulp cooked from a blend of stalks and silique valves and from stalks only (Table I). While for pulp from stalks the polydispesity coefficient of 1.1 was calculated, the pulp from straw including silique valves is characterised by the polydispesity coefficient of 2.5 which can lead to greater local heterogeneity in the pulp bed having a considerable impact on the exit profile of alkali lignin displaced from the bed.

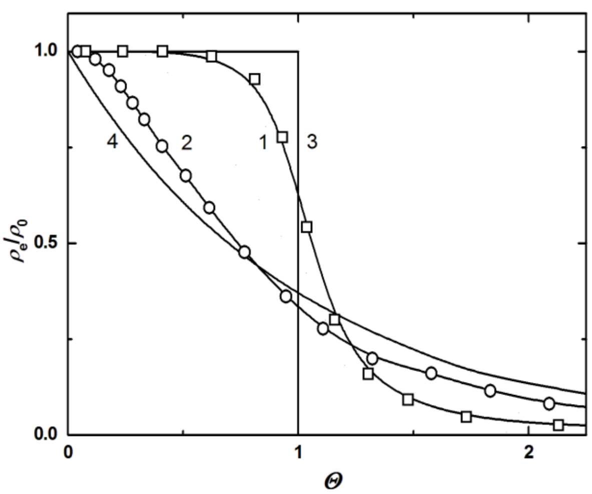

Figure 1. Typical breakthrough washing curves for soda pulp: Pe = 42.5 (line 1), Pe = 3.1 (line 2), plug flow (line 3), perfectly mixed flow (line 4).

It is worth mentioning that soda pulp bed manifested greater hydraulic resistance in comparison with kraft pulp from hardwood, even through both rapeseed pulp and hardwood pulp rank among short-fibred pulps. The hydraulic resistance measured at the bed consistency of 90 kg m^{-3} was found to be 9×10^6 Pa s m^{-1} and 14.2×10^6 Pa s m^{-1} for pulp from stalks only and from straw with silique valves, respectively, while only 2.9×10^6 Pa s m^{-1} for pulp cooked from a blend of hardwoods in our preceding paper[9]. Thus, hydraulic resistance measurements showed that the washing of soda pulp cooked from rapeseed straw can bring some problems in the displacement washing zones of vacuum drum filters where the pressure difference is the driving force of displacement process.

Wash yield

The displacement washing curve area is directly proportional to the amount of alkali lignin removed from the bed. Replacing the dimensionless time, *Θ*, by the wash liquor ratio, RW, defined as the mass of wash liquid passed through the bed to the given time divided by the mass of mother liquor originally present in the bed, the traditional wash yield, $WY_{\mathrm{RW=1}}$, can be expressed as

$$WY_{\mathrm{RW=1}} = \frac{\int_{\mathrm{RW=0}}^{\mathrm{RW=1}} \frac{\rho_e}{\rho_0}\, \mathrm{d}(RW)}{\int_{\mathrm{RW=0}}^{\mathrm{RW}\to\infty} \frac{\rho_e}{\rho_0}\, \mathrm{d}(RW)} \tag{4}$$

Thus, the traditional wash yield is defined as the amount of a solute washed out at *RW* = 1 divided by the total amount of a solute removed from the pulp bed during the washing run.

Influence of the Péclet number on the wash yield for soda pulp is shown in Fig. 2. For comparison, the results obtained in the previous paper[9] for displacement washing of pulp from hardwoods are also illustrated in Fig. 2. In spite of the scatter in the data, it is evident that the wash yield increases with the increasing Péclet number. Similarly as for hardwood pulp, the experimental points are located below the curve derived for the packed bed of non-porous particles by Brenner[10]. The reason is that, for packed bed of non-porous particles, the washing process is reduced to the displacement mechanism accompanied by interfacial mixing between displaced and displacing fluids. However, in case of a packed bed of compressible porous particles in the swollen state, like pulp fibres, the leaching may play a significant role mainly in the spaces of the pulp bed in which the interparticle pores were filled up with the wash liquid and the concentration driving force enables the transfer of lignin macromolecules from the fibre walls towards the wash liquid.

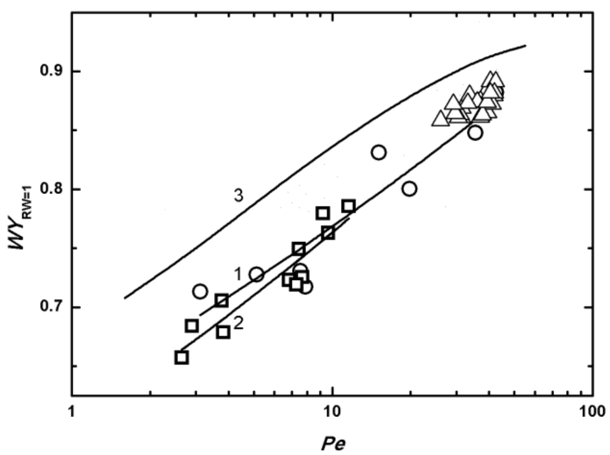

Figure 2. Displacement wash yield as a function of the Péclet number for soda pulp from blend of stalks and silique valves (○), and from stalks only (□), for kraft hardwood pulp[9] (△), Eq. (5) (line 1), Eq. (6) (line 2), Eq. (7) (line 3).

The Péclet number characterizing the dispersion of lignin in the pulp bed is influenced not only by leaching mechanism, but also by the heterogeneity of the porous medium when the fluctuations in the pore-water velocity have probably dominant impact on the variations in the dispersion of lignin in soda pulp beds.
Based on our own data measured for the soda pulp bed, the following equation was derived for the quantitative evaluation of the effect of wash liquid dispersion on the wash yield

$$WY_{\mathrm{RW=1}} = 0.627\, Pe^{0.0879} \quad (5)$$

for the soda pulp cooked from rapeseed straw containing stalks and silique valves. The suitability of Eq. (5) was evaluated on the basis of the mean relative quadratic deviation of the wash yield which was 2.8 %. Values of the Péclet number varied in the relative wide range of 3.1 to 42.5. Since the values of regression coefficients, evaluated by the least square method, represent an estimate of the real values, the 95% confidence intervals were also calculated for the coefficient of 0.627 ± 0.020 and for the power of the Péclet number of 0.0879 ± 0.0123.
For soda pulp cooked from stalks only, when the Péclet number varied in the relative narrow interval from 2.6 to 11.6, the correlation was derived in the form

$$WY_{\mathrm{RW=1}} = 0.599\, Pe^{0.105} \quad (6)$$

with the mean relative quadratic deviation of 1.9 %. The 95% confidence intervals for the coefficient and the power of the Péclet number were 0.599 ± 0.010, and 0.105 ± 0.009, respectively. Presumably, lower values of the Péclet number covering the range from 2.6 to 11.6 measured for pulp cooked form stalks only represent more bridgings between the fibres and greater variations in local voidages which promote the channelling phenomenon.
For comparison with the correlations, Eqs. (5), and (6) for soda rapeseed pulps, the theoretical wash yield of the displacement in a packed bed of non-porous particles calculated according to Brenner[10] was expressed as a function of the Péclet number in the form

$$WY_{\mathrm{RW=1}} = 0.695\, Pe^{0.0763} \quad (7)$$

for the Péclet number within the range from 2.4 to 40.

Conclusions

Packed bed of pulp fibres is a very tangled system with randomly oriented porous, compressible particles with different size and a central cavity known as lumen. Even under strictly identical experimental conditions, the bed of fibres was always different, at least with various local porosities. Thus, the properties of pulp fibres along with their spatial configuration substantially affect the flow of wash liquid through the pulp bed and have a noticeable impact on the shape of the displacement washing curve describing the lignin removal from the soda pulp bed.
In spite of these facts, the results obtained showed that the wash yield for soda rapeseed pulp was lower in comparison with kraft pulps cooked from softwoods[11] and hardwoods[9]. Hydraulic resistance of the soda pulp bed is much greater than that of hardwood and softwood pulps. Mechanical dispersion is primarily caused by local variations of the water flow velocity due to the intrinsic heterogeneity of the porous medium. However, it seems that the presence of silique valves in rapeseed straw has no significant influence upon the washing efficiency and contributes to shorter mean residence time of lignin washed out of the pulp bed.
Nevertheless, to obtain relevant information on the displacement washing of soda pulp cooked from rapeseed straw, further studies on pulps produced at various degrees of their delignification should be carried out.

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Symbols

D axial dispersion coefficient, $m^2 s^{-1}$
h thickness of bed, m
Pe Péclet number based on bed thickness defined by Eq. (3)
RW wash liquor ratio
t time from start of experiment, s
t_m mean residence time defined by Eq. (2), s
u wash liquid superficial velocity, $m s^{-1}$
$WY_{RW=1}$ wash yield at $RW = 1$ defined by Eq. (4)

Greek letters

δ mean relative 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 porosity of packed bed
Θ dimensionless time defined by Eq. (1)
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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