RAPESEED STRAW AS A POSSIBLE SOURCE OF NON-WOOD FIBRE MATERIALS

FRANTIŠEK POTŮČEK and MILOSLAV MILICHOVSKÝ

University of Pardubice, Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials, 532 10 Pardubice, Czech Republic

Received July 14, 2010

Rapeseed straw was tested as a non-wood raw material for the production of cellulosic pulps. Preliminary soda pulping experiments showed suitable cooking conditions, *viz*. a liquor-to-raw material ratio of 5:1, an active alkali charge of 17%, a cooking temperature of 160 ºC, and an H-factor of 900 h were sufficient to produce pulp with a low content of rejects. Under these conditions, a total pulp yield of 37.1%, a kappa number of 38.3 and an amount of rejects of 1.1% were achieved. The chemical composition of rapeseed straw was also determined. The bonding and strength properties of pulp fibres exhibiting good beatability were evaluated by a simple rheosedimentation method and by measuring tensile strength.

Keywords: rapeseed straw, chemical composition, soda pulping

INTRODUCTION

Non-wood based raw materials, such as annual crops, can be applied as an effective alternative to the ever-decreasing forest wood resources in most developing regions. While in Asia non-wood fibres represent a substantial raw material for papermaking, in some European regions they form a very low part in pulp and paper production. Furthermore, in some countries, there is plenty of land not utilized for food production, which might be suitable for cultivation of plants for industrial purposes. A better utilization of the yearly renewable resources (*e.g*., wheat straw,[1-4] hemp,[5-10] rice straw,[11] industrial grass,[12] cardoon,[13] kenaf,[14] flax,[8,10] okra stalks,[15] bamboo,[16] amaranth,[17] orache,[17] Jerusalem artichoke,[17] etc.) is an important aspect in the context of sustainable development. Non-woody pulp has been traditionally used as a raw material for the production of common, writing and printing paper, as well as for specialty papers like bible, filter, cigarette, currency, insulating and condenser paper.

Besides kraft[1,5,11,13] and kraft-AQ[13] pulping – the most important processes currently applied for cellulosic fibre production from wood – and bisulpite and neutral sulphite treatment,[5] sulphur-free pulping processes, such as soda,[9,11,15,16] soda-AQ,[11-13,15,17] and alkaline oxygen,[5] have been frequently applied for annual and perennial plants. Autocatalyzed ethanol pulping of hemp has been investigated by Zomers *et al*.[6] Also, the enzymatic mechanical process for pulping of bast fibres of flax and hemp, based on a treatment with cellulolytic and pectinolytic enzymes, has been developed by Ekbland *et al*.[10] To solve the environmental pollution problem caused by the black liquor produced in papermaking industry, a new method of wheat straw pulping with aqueous ammonia containing a small amount of caustic potash as a cooking liquor has been reported by Huang *et al*.[2,3] In this case, the black liquor is no longer a pollutant, instead it can be used as a fertilizer for agriculture.

Rapeseed ranks among ten most important plants in the world and its world production is growing rapidly. Globally, rapeseed is the third most important oilseed crop after soybean and palm; it is currently used for biodiesel applications as well, but its range of applicability could be extended in the pulp and paper industry as one of the annual fibre crops. In the present work, the suitability of rapeseed straw for cellulosic fibre production under conventional soda

pulping was examined. The resulting pulp was analysed as to yield, rejects, kappa number and bonding abilities of the pulp fibres.

EXPERIMENTAL

Rapeseed straw (*Brassica napus*) from Bohemian-Moravian Highlands was used for pulping. Before cooking, the foreign materials and remains of grains were removed and then rapeseed straw was cut to a length of 30 mm. The raw materials consisted mainly of stalks, but approximately one third of the total amount was formed of valves of silique.

At first, the chemical analysis of rapeseed straw was made according to Tappi Test Methods.[18] Ash (TAPPI T 211 om-02) and silica (TAPPI T 245 cm-98) contents were determined, as well as the extractives contents, tannin (TAPPI T 204 cm-97) – by Soxhlet extraction with ethanol, resin with a 2:1 mixture of benzene-to-ethanol by volume, and Klason lignin (TAPPI T 222 cm-02) using 72% sulphuric acid, in stalks of different diameters, and in the valves of silique, after milling the randomly taken samples in a laboratory vibratory mill to powder. The holocellulose content was calculated for a total sum of 100%. The water solubility of the raw material was determined in accordance with the TAPPI Test method T 207 om-93, while the 1% sodium hydroxide solubility – according to TAPPI T 212 om-88.

Before cooking experiments, the rapeseed straw was stored in the laboratory. The moisture content of straw was of 7 to 9%, depending on the relative humidity of air. Soda pulping runs were conducted in 6 batch reactors, each with a capacity of 750 cm^3, immersed in an oil bath. The mass of o.d. rapeseed straw in each reactor was of approximately 40 g. On the basis of trial pulping experiments carried out for a liquor-to-raw material ratio ranging from 3:1 to 5:1, an alkali charge ranging from 13 to 19% and a cooking temperature between 160 and 165 ºC were selected as cooking conditions, when the amount of rejects was acceptable. Hence, subsequent batch cookings, giving pulps for handsheet production, were performed at a liquor-to-raw material ratio kept at 5:1, an alkali charge of 17%, expressed as Na_2O per o.d. raw material, and cooking temperature of 160 ºC. The temperature regime was as follows: 20 min heating to 70 ºC, 20 min dwelling at 70 ºC, 45 min heating to 160 ºC, and then dwelling at cooking temperature. The batch cooks were ended as soon as the H-factor reached a value between 500 and 1500 h. The corresponding pulping time at cooking temperature varied from 65 to 215 min. The time dependencies of both temperature and H-factor are illustrated in Figure 1.

After the soda cooking process, the cooked pulp was refined, thoroughly washed and screened with a 10-mesh sieve. When the H-factor reached 900 h, the pulp prepared at a cooking temperature of 160 ºC and an alkali charge of 17% as Na_2O was beaten in a laboratory ring beater to a beating degree of 66 SR, determined by the Shopper-Riegler method – according to the ISO 5267-1 standard. Handsheets from this pulp were made on a handsheet machine and tested as to the strength properties. Paper-forming abilities of unbeaten and beaten pulps were evaluated by the simple rheosedimentation method.[19] For unbeaten and beaten pulps prepared under laboratory-scale conditions, both rheosedimentation parameters, *i.e.* standard rheosedimentation velocity and final concentration of sediment characterizing sedimentation of the fibre network were determined by monitoring the height of the fibre network in a cylindrical vessel. The tensile length of the handsheets prepared from unbeaten and beaten pulps was measured on a TIRAtest 26005 device. For every handsheet with a constant grammage of 95 g m^{-2}, tensile strength was determined at least 10 times.

RESULTS AND DISCUSSION

Chemical composition

The chemical composition of the raw materials has a considerable impact on both pulp yield and fibre properties. Table 1 compares the results measured for rapeseed with those published in literature[1,2,4,6,8,11,12,14,16,17] for other non-wood crops, as well as for hardwoods[20] and softwoods.[20] The chemical composition of rapeseed straw was determined for random samples, as well as for the main components, such as valves of silique and stalks with a diameter below 2 mm, between 2-5 mm, and above 5 mm. The highest content of ash and extractives was found for valves of silique, while for stalks, the contents of ash and extractives decrease with increasing stalk diameter. On the contrary, the valves of silique evidence the lowest content of lignin, which slightly increases with an increasing diameter or age of the stalks. Similarly to other non-wood crops, the ash content of rapeseed is much higher than that of hardwoods[20] or softwoods.[20] It is worth mentioning that silica forms 36.9% of the ash, *i.e*. the silica content was of 3.2%. For wheat straw, Deniz *et al*.[1] and Huang *et al*.[2] reported silica contents of 4.23, and 4.59%, respectively, while Fišerová *et al*.[17] found out a silica content of 0.03, 0.08 and 0.16%

for amaranth, orache and Jerusalem artichoke, respectively. It is generally known that the presence of silica in spent pulping liquor leads to problems in pulping, *e.g.* a poor drainage of pulp during paper making and difficulties in the chemical recovery of the spent liquor.

The lignin content can influence the reaction times of delignification in the digester, or reagent concentration. As shown in Table 1, the lignin content of rapeseed straw was of 15.52%. Approximately similar values – 15.3, 17 and 14.77% – were found for wheat straw,[1] industrial grass,[12] and Jerusalem artichoke,[17] respectively. It is evident that the lignin content of rapeseed straw is substantially lower than that of hardwoods[20] and softwoods,[20] as well as that of most other non-wood crops (Table 1).

Table 1
Chemical composition (in mass %) of rapeseed straw *versus* literature data [1,2,4,6,8,11,12,14,16,17,20]

Raw material	Ash	Extractives	Lignin	Holocellulose	Cold water	Hot water	1% NaOH
Rapeseed straw							
Valves of silique	11.47	23.20	11.66	53.68	–	–	–
Stalks below 2	8.09	17.76	16.09	58.07	–	–	–
mm	7.41	15.35	16.60	60.65	–	–	–
Stalks 2-5 mm	7.08	14.11	16.99	61.72	–	–	–
Stalks above 5	8.80	17.16	15.52	58.51	12.53	13.35	34.9
mm							
Random sample							
Wheat straw[1]	4.7	–	15.3	74.5	10.75	13.99	40.59
Wheat straw[2]	–	–	26.43	–	–	–	–
Wheat straw[4]	8.23	–	21.6	72.94	–	9.3	40.1
Hemp[6]							
Core	4.5	8.9	21.8	–	–	–	–
Bast	5.9	11.9	3.0	–	–	–	–
Hemp[8]							
Core	6	9	~22.5	~60	–	–	–
Bast	5	12	2.9	~77.5	–	–	–
Rice straw[11]	9.2	–	21.9	60.7	–	7.3	50.7
Industrial grass[12]	3.5	–	17	67	–	15	–
Kenaf[14]	< 1	–	–	–	–	–	–
Flax[8]							
Core	–	10	~27.5	~65	–	–	–
Bast	1	3.6	5.1	~90	–	–	–
Bamboo[16]							
O. abyssinica	4.6	–	23.4	–	–	5.8	22.1
Bambusa vulgaris	2.3	–	21.7	–	–	0.7	23.5
Amaranth[17]	11.70	30.06	13.18	26.10	23.49	–	46.84
Orache[17]	1.97	8.40	19.53	38.87	4.58	–	27.55
Jerusalem artichoke[17]	3.15	33.91	14.77	23.10	26.48	–	48.50
Oak[20]	0.55	10.54	21.37	67.54	–	–	–
Beech[20]	0.64	2.64	24.47	72.25	–	–	–
Spruce[20]	0.41	2.70	30.44	66.45	–	–	–
Pine[20]	0.25	10.37	29.53	59.85	–	–	–

Water can extract inorganic compounds, monosaccharides, oligosaccharides, alcohols, colouring matters, tannin agents and some low molecular mass phenols,[17] which could consume the cooking reagents. For rapeseed straw, hot water solubility is slightly higher than cold water solubility, approximately similar to that of wheat straw,[1] higher than that of rice straw,[8] bamboo[16] and orache,[17] but lower than that of industrial grass,[12] amarant[17] and Jerusalem artichoke.[17] Solubility in 1% NaOH was much higher

than in water. It can be assumed that the substances removed from the annual plants by extraction with sodium hydroxide also contain, besides most of the extractives, cell-wall materials.[17] Based on its high value, 34.9%, rapeseed straw can be expected to provide a low pulp yield. In comparison to literature data, rapeseed solubility achieved in 1% NaOH was lower than that of wheat straw,[1,4] rice straw,[8] amaranth[17] and Jerusalem artichoke,[17] but higher than that of bamboo[16] and orache.[17]

Soda pulping

The soda pulping process without sulphur compounds is frequently applied to non-wood fibre materials. Therefore, it was chosen for laboratory pulping of rapeseed straw.

Trial cooks showed that a cooking temperature of 160 ºC is sufficient, at a liquor-to-raw material ratio of at least 5:1. Under these conditions, an alkali charge of 17% Na_2O on o.d. raw material appears to be suitable, mainly with respect to small amounts of rejects. The cooking temperature and liquor-to-raw material ratio applied were the same as those reported by Atik[15] and Fišerová *et al.*,[17] respectively. In soda or soda-AQ processes, a higher cooking temperature, ranging between 165 and 170 ºC, was used to cook industrial grass,[12] hemp,[9] bamboo,[16] amaranth,[17] orache[17] and Jerusalem artichoke,[17] a temperature of 180 ºC being applied to cook rice straw.[11] The alkali charge is comparable with that for undepithed amaranth[17] and bamboo,[16] in a soda-AQ process.

H-factor values were used to compare cookings at varying reaction times and temperatures in a more meaningful manner (Fig. 1). The H-factor is a cooking variable that combines cooking temperature and time into a single variable that indicates the extent of reaction. H-factor values were derived using Vroom's equation.[21] Figure 2 plots the percent total pulp yield and kappa number as a function of the H-factor. Both variables drop with increasing the H-factor, which is directly proportional to the cooking time. Figure 2 shows that, at an H-factor over 1000 h, the drop in kappa number, expressing the degree of delignification, is less steep. Also, the amount of rejects is not strongly influenced by the cooking time in the interval of the H-factor from 900 h to 1500 h, as illustrated in Figure 3. At a H-factor equal to 900 h, a total pulp yield of 37.1%, kappa number of 38.3, and amount of rejects of 1.1% were achieved. The pulp yield is comparable with those reported for the bamboo[16] species *Bambusa vulgaris* (37.3% at kappa number of 21.9), rice straw[11] (36.99% at kappa number of 15.89), and orache[17] (37.7% at kappa number of 20). The pulp yield of rapeseed straw is higher than that of amaranth (34.4%) and Jerusalem artichoke (27.7%), as found by Fišerová *et al.*,[17] while Hernadi *et al.*[12] reported a pulp yield of 49.5% at a kappa number equal to 12.1 for industrial grass.

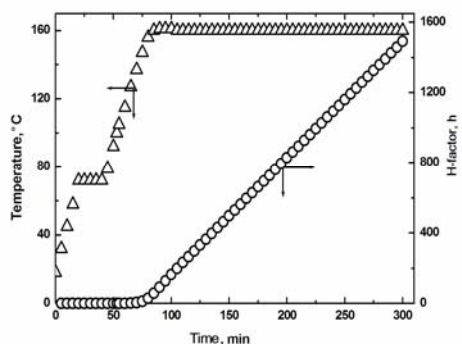

Figure 1: Time dependences of temperature and H-factor for soda pulping

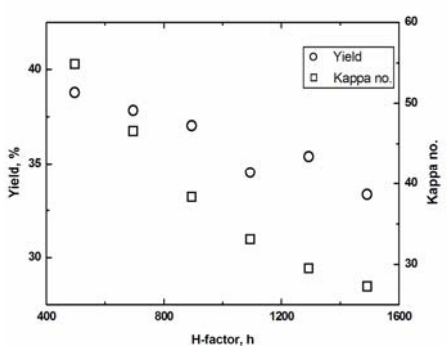

Figure 2: Total yield and kappa number as a function of H-factor (liquor-to-raw material ratio – 5:1, alkali charge – 17% as Na_2O, cooking temperature – 160 ºC)

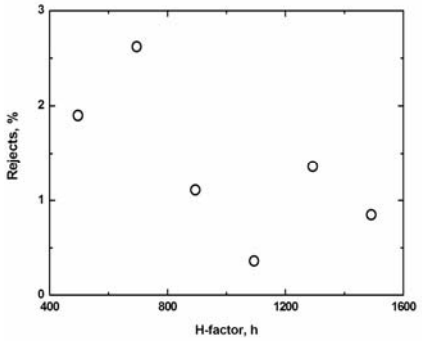

Figure 3: Amounts of reject as a function of H-factor (liquor-to-raw material ratio – 5:1, alkali charge – 17% as Na_2O, cooking temperature – 160 ºC)

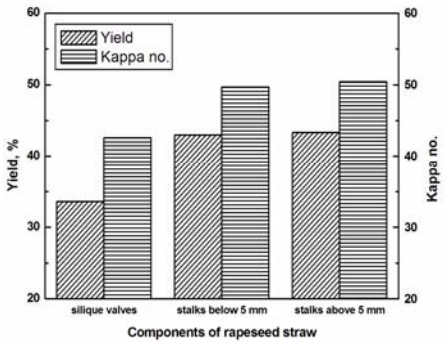

Figure 4: Total yield and kappa number of silique valves and stalks with a diameter below and above 5 mm (cooking temperature – 165 ºC, H-factor – 700 h)

Table 2
Fibre properties of unbeaten and beaten pulp cooked from rapeseed straw at H-factor = 900 h

Pulp	Beating degree, SR	Sedimentation velocity, mm s^{-1}	Sediment concentration, kg m^{-3}	Tensile length, km	Tensile index, N m g^{-1}	Relative elongation, %
Unbeaten	33	4.75	10.62	3.17	31.1	1.4
Beaten	66	1.09	6.67	6.92	67.9	2.0

It has to be reminded that the total pulp yield and kappa number, as well as the amounts of rejects are influenced by the content of valves of silique and stalks with different diameter in the random samples of raw material to be inserted into reactor vessels. The total yield and kappa number of some components of rapeseed straw, *i.e.* valves of silique, stalks below and above 5 mm in diameter, are illustrated in Figure 4. Comparable total yields and kappa numbers were found for stalks. The lowest pulp yield, kappa number and amount of rejects were attained by valves of silique. The amounts of rejects were of 0.1, 1.4 and 0.9% for valves of silique, stalks with a diameter below 5 mm, and stalks with a diameter above 5 mm, respectively.

Pulp properties

The pulp cooked to an H-factor of 900 h, when cooking temperature was maintained at 160 ºC and the active alkali charge was of 17% (as Na_2O) comprised too long fibre bundles, of as much as 2 cm in length. To investigate fibre properties, the pulp was beaten in a laboratory ring beater. The pulp prepared from rapeseed straw showed good beatability. For a short beating time (approx. 2 min), the beating degree increased from 33 SR – a value measured for unbeaten pulp – to 66 SR.

Knowledge on the bonding and strength properties of pulp fibres is a key demand for a well-controlled papermaking process. Both of them permit estimations by the so-called rheosedimentation method,[19] *i.e.* by observation and evaluation of the typical phenomenon of diluted pulp slurries with appropriate papermaking properties during their sedimentation. Two basic parameters of rheosedimentation, the standard rheose-dimentation velocity and the final concentration of sediment (Table 2) were evaluated for unbeaten and beaten pulps. The results obtained showed that, with increasing the beating degree, the standard rheosedimentation velocity, as well as the final concentration of sediment decrease. This can be explained by the fact that the volume of water molecules loosely bound to the fibre surface by hydrogen bonds increases with increasing the beating degree. It was confirmed that both parameters depend on the hydratation ability of fibre components in pulp suspension and decrease with increasing hydratation ability. The standard rheosedimentation velocity and, particularly, the final concentration of sediment measured for rapeseed beaten pulp are comparable with those reported by Fišerová *et al.*[22] (1.8 mm s^{-1} and 6.95 kg m^{-3}, respectively) for bleached pulp

prepared from a blend of hardwoods. Milichovský and Češek[19] obtained a standard sedimentation velocity of 1.2 and 1.7 mm s^{-1}, respectively, for sulphate bleached softwood pulp (a blend of spruce and pine) and bleached spruce pulp, as well as final sediment concentrations of 5.7 and 7.2 kg m^{-3} for sulphate bleached Eucalyptus hardwood and bleached beech pulp, respectively.

Table 2 also summarizes the tensile length and index, along with the relative elongation measured for unbeaten and beaten rapeseed pulp. The average values of the tensile length and index given in Table 2 were calculated for a mean relative deviation of 3.7 and 4.5% for unbeaten and beaten pulps, respectively. With increasing the beating degree, the tensile index and relative elongation increase. These results confirmed unambiguously the relations between tensile index, on the one hand, and standard rheosedimentation velocity and final sediment concentration, on the other, measured for unbleached and bleached hardwood kraft pulp by Fišerová *et al*.[22] The tensile index found for beaten rapeseed pulp is more or less comparable with that for hemp[9] (73.74 N m g^{-1}), amaranth[17] (69-71 N m g^{-1}), and Jerusalem artichoke[17] (68-70 N m g^{-1}). Lower values of the tensile index were reported for hemp (51 N m g^{-1}) and flax (54 N m g^{-1}) by de Jong *et al*.,[8] for orache (59-60 N m g^{-1}) by Fišerová *et al*.,[17] for wheat straw (43.2 N m g^{-1}) by Hung *et al*.,[2] and for rice straw (breaking length of 2.664 km and 2.439 km, depending on the cooking conditions of the soda process, and of 3.494 km for soda-AQ process) by Rodríguez *et al*.,[11] while higher values of the tensile index were reported for wheat straw (82 N m g^{-1}) by Garg *et al*.[4] and also higher values of breaking length, of 8.16 to 10 km, as depending on the kraft pulping conditions, by Deniz *et al*.[1]

On the basis of the preliminary results obtained in this work, one can, therefore, conclude that rapeseed straw could be a potential source of raw material for pulp and paper industry. However, further studies should be developed to confirm the suitability of rapeseed as a future non-wood fibre source.

ACKNOWLEDGEMENTS: This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, under Research Project MSM0021627501.

REFERENCES

[1] İ. Deniz, H. Kirci and S. Ates, *Ind. Crop. Prod*., **19**, 237 (2004).
[2] G. Huang, C. Zhang and Z. Chen, *Chinese J. Chem. Eng*., **14**, 729 (2006).
[3] G. Huang, J. X. Shi and T. A. G. Langrish, *Bioresour. Technol*., **98**, 2829 (2007).
[4] M. Garg, A. K. Gautam and S. P. Singh, *IPPITA J*., **20**, 113 (2008).
[5] I. Kovacs, A. Rab, I. Rusznak and S. Annus, *Cellulose Chem. Technol*., **26**, 627 (1992).
[6] F. H. A. Zomers, R. J. A. Gosselink, J. E. G. van Dam and B. F. Tjeerdsma, *Tappi J*., **78**, 149 (1995).
[7] F. Correia, D. N. Roy and K. Goel, *Pulp Pap.-Can*., **99**, T303 (1998).
[8] E. de Jong, G. J. van Roekel, M. H. B. Snijder and Y. Zhang, *Pulp Pap.-Can*., **100**, T270 (1999).
[9] D. Dutt, J. S. Upadhyaya, R. S. Malik and C. H. Tyagi, *Cellulose Chem. Technol*., **39**, 115 (2005).
[10] C. Ekblad, B. Pettersson, J. Zhang, S. Jernberg and G. Henriksson, *Cellulose Chem. Technol*., **39**, 95 (2005).
[11] A. Rodríguez, A. Moral, L. Serrano, J. Labidi and L. Jiménez, *Bioresour. Technol*., **99**, 2881 (2008).
[12] A. Hernadi, I. Lele, A. Rab, A. Vig, G. Lepenye, J. Janowszky and B. Brochier, in *Procs. International Symposium Challenges of Pulp and Papermaking Technology*, Bratislava, November 8-10, 2006.
[13] S. Abrantes, M. E. Amaral, A. P. Costa and A. P. Duarte, *Bioresour. Technol*., **98**, 2873 (2007).
[14] A. F. Kaldor, C. Karlgren and H. Verwest, *Tappi J*., **73**, 205 (1990).
[15] C. Atik, *Cellulose Chem. Technol*., **36**, 353 (2002).
[16] P. Khristova, O. Kordaschia, R. Patt and I. Karar, *Cellulose Chem. Technol*., **40**, 325 (2006).
[17] M. Fišerová, J. Gigac, A. Majtnerová and G. Szeiffová, *Cellulose Chem. Technol*., **40**, 405 (2006).
[18] Tappi Test Methods, Atlanta, Georgia, Tappi Press, 2004.
[19] M. Milichovský and B. Češek, *Cellulose Chem. Technol*., **38**, 385 (2004).
[20] F. Potůček and J. Miklík, *Chem. Pap*., **64**, 147 (2010).
[21] L. Šutý, Výroba a vlastnosti buničín, Alfa Bratislava/SNTL Praha, 1982.
[22] M. Fišerová, J. Gigac and J. Balberčák, *Pap. Celul*., **64**, 362 (2009).