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Research Article

Neutral sulfite semi-chemical pulping of rapeseed residues

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Abstract: Neutral sulfite semi-chemical (NSSC) pulping of rapeseed residues from Karadj rapeseed growing fields was investigated. Rapeseed residue was collected from the research field at the Agriculture and Natural Resources Campus, University of Tehran located in Karadj. Cellulose, lignin, holocellulose, extractives soluble in alcohol acetone, 1% NaOH solubility, and ash were determined as 42 ± 2%, 17 ± 1%, 77.5 ± 2%, 2.2 ± 0.1%, 50.3 ± 1.6%, and 6%, respectively. Fiber length, width, and cell wall thickness were measured as 1.190 mm, 32 µm, and 4 µm. Three pulping durations of 20, 40, and 60 min and 5 chemical charges of 8%, 10%, 12%, 14%, and 16% active alkali were used. Cooking temperature at 175 °C, Na_2SO_3 to Na_2CO_3 ratio of 3:1, and liquor to residue ratio of 8:1 were kept constant. The highest yield (72%) was obtained applying the treatment combination of 20 min pulping time and 8% active alkali and the lowest yield (58.7%) was observed with 60 min pulping time and 16% chemical. After the pulping study, selected pulps were refined to 375 ± 5 mL CSF and 60 gm^{-2} handsheets were made. The results of pulping and handsheet evaluation indicated that 12% active alkali, 60 min pulping at 175 °C can be considered as the optimum pulping condition for rapeseed residues. Tear, tensile, and burst indices and breaking length of this pulp were measured as 7.5 mN m^2g^{-1}, 66.5 N mg^{-1}, 2.57 kPa m^2g^{-1}, and 6.78 km, respectively.

Key words: Rapeseed, NSSC, yield, strength, optical, fiber length

Introduction

Paper was invented using non-wood fibers, and in the course of its expansion from Samarkhand to Middle East to Europe non-wood fibers are still in use. However, in Europe, due to the availability of vast forests and wood supply, the status of paper fibrous raw material changed and wood is primarily utilized. However, during late 20th century, global shortage of wood emerged and consequently paper industry was forced to look for new alternatives for fibrous raw material. Furthermore, the fiber supply in regions like Asia and Middle East is so tense that these locations concentrated on utilization of non-woods as raw material. Iran is concentrating on rapeseed plantation to produce vegetable oil for its growing population. Then, very good supply of residues will be available. These residues, on the contrary to other agricultural residues, such as wheat and rye straw, which is usually

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used as cattle feed, is extremely coarse and cannot be used as cattle feed, even after employing all sorts of preparation. Therefore, it will be available as raw material for pulping.

Paper industry worldwide is facing shortage of suitable fibers and this limitation is not only the issue for fiber deficient countries but also North America as well as Europe has started considering non-wood fiber utilization (Mackean and Jacobs 1997; Paavilainen 1998). Therefore, non-wood pulping picked up the momentum during the last 40 years and the share of non-wood pulp increased from 7% to 12% (Ates et al. 2008). This large increase in non-wood pulp production motivated research activities worldwide and various research groups initiated works to improve non-wood pulping. Such research covers a wide range from conventional soda pulping of bagasse and cereal straw to reeds and bamboo to even date palm tree branches and rachises (Khristova et al. 2005). Even though bagasse and cereal straw pulping has reached its mature stage, it still faces limitations, such as non-selectivity of lignin removal and changes in lignin structure, adverse environmental effects, and finally yet importantly, the low yield after bleaching. Various alternative pulping processes including neutral sulfite pulping of wheat straw (Ali et al. 1991), and soda/AQ, alkaline sulfite/AQ, and ASAM pulping of date palm residues (Khristova et al. 2005) were investigated. Application of 6 different pulping processes (Kraft-AQ with either low or high alkali, bio-kraft, soda/AQ, alcell, and formacell) was tested on Turkish wheat straw and promising results were reached (Ates et al. 2008). Alkaline sulfate/AQ pulping and totally chlorine free bleaching were applied on wheat straw, rice straw, and bagasse to develop an alternative pulping for these materials (Hedjazi et al. 2008a, 2008b, 2009). Other pulping processes have been studied to increase the pulping yield. Wheat straw alkaline peroxide mechanical pulping (APMP) (Pan & Leary 2002), APMP pulping of bagasse and kenaf (Xu and Rao 2001) and chemi-mechanical pulping of kenaf (Law et al. 2003) are the most recent examples.

To the best of our knowledge, no activity is available on rapeseed pulping worldwide and only research groups in Iran showed interest in this subject. Soda pulping of rapeseed residue was tested by Sefidgaran (2003) in an attempt to use the produced pulp in corrugating paper production and Azadfallah (unpublished data) applied APMP pulping on this raw material. Since suitable amount of unutilized rapeseed residue is available at different locations in Iran, the objective of this study was to develop application of neutral sulfite pulping process on this valuable raw material.

Materials and methods

Sampling

Rapeseed residue was collected at the Agriculture and Natural Resources Campus Experimental Station, University of Tehran. Samples were cleaned and leaves and debris were separated, and then the stems were depithed carefully by hand. Depithed material was cut into 2-4 cm length chips. Chips were dried at ambient temperature, and after reaching equilibrium moisture content, chips were stored in plastic bags until used.

Fiber dimension and chemical analysis

Small pieces of stems were defibrated using the technique developed by Franklin (1954) and then the dimensions of 100 fibers were randomly measured using a projection microscope and the average of the measurements was calculated.

Relevant Tappi test methods were used for chemical analysis as follows: Sample preparation; T267-om 85: Moisture determination; T264-om 88: Ash; T211-om 93: Extractives soluble in alcohol-acetone; T207-om 97: Extractive free powder; T264-om 97: Cellulose; T264-om 88: Lignin; T222-om 97: Holocellulose; Useful method 249- um 75: 1% NaOH solubility; T212-om 98.

Pulping

Five levels of active alkali at 8%, 10%, 12%, 14%, and 16% (based on NaOH) and 3 pulping durations of 20, 40 and 60 min were employed, and for each combination of variables, 3 replica pulps were prepared. Sodium sulfite-sodium carbonate ratio at 3:1 and pulping temperature of 175 °C were kept constant. The cooking trails were performed using a 6-cylinder rotating digester, using 100 grams of depithed residue in each trial, and pulping time was measured after reaching pulping temperature. At the end of each cook, the content of each cylinder was discharged on 200 mesh screen and the cooked material was washed using hot water and the remaining liquor was separated by hand pressing the cooked material. Digester yield was measured using the weight of the washed material on top of the screen without defibration. Cooked material was defibrated using a 25 cm laboratory single disc refiner, and then the pulp was screened using a set of 2 screens, a 14-mesh screen on top of a 200 mesh screen. Material remained on the 14 mesh screen was considered as reject (shives) and the fibers passed the 14 mesh screen and remained on the 200 mesh screen was considered as accept (screened yield). Defibration yield was measured after refining and screening of the cooked material.

Following Tappi test methods were used for pulp analysis: Kappa number; T236-om 99: Beating; T248-om 88: Freeness; T227-om 99: Handsheet preparation; T205-om 95: Basis weight; T401-om 88: Caliper; T411-om 89: Tear strength; SCAN p11:73: Tensile strength and breaking length; T204-om 92: burst strength; T403 om-02: brightness T452 om-08 and opacity; T425 om-06.

Results

Chemical composition and fiber dimensions: The percentage of cellulose, lignin, hollocellulose, extractive soluble in alcohol-acetone,1% NaOH solubility and ash is summarized in Table 1 and the fiber dimensions as well as calculated runkel, felting and flexibility coefficients are summarized in Table 2. Each value in Table 1 is the average of 3 measurements and each value in Table 2 is the average of 100 measurements. Standard deviation of the measurements is also given in both tables to show the variations of the given property.

Pulping measurements

Both digester and defibration yield are measured separately and summarized in Table 3. Our experience indicates that during defibration, some fines are generated and these fines can pass the 200 mesh screen. Therefore, to show the yield which is usually obtained in industrial practices, the digester yield is better indication of the actual yield. The screened yield as well as reject is also given in Table 3. The results exhibited that higher chemical charge as well as pulping time reduces both digester yield and defibration yield. It should be noted that defibration usually reduces the pulping yield. This is the consequence of fine generation and the presence of pith particles which are very short and small cubical. However, without defibration, such fine generation is limited. Statistical analysis indicated that the effect of either chemical charge or cooking duration as well as the combined effect of both variables on digester and defibration yields is statistically significant at 99% level. Therefore the Duncan Multiple Range Testing ranking of the averages are calculated and shown in Table 3.

Pulp strength

NSSC pulping behavior of rapeseed residues was evaluated and pulps produced applying different charges of active alkali at 20 min pulping time and 175 °C temperature were selected for strength evaluation. Furthermore, in order to demonstrate the effect of pulping time, constant active alkali charge of 12% and 3 pulping times were selected as well. The results of

Table 1. Chemical composition of the rapeseed residues.

Component	Value %	Coefficient of Variation %
Cellulose	43 ± 2	4.65
Lignin	17 ± 1	5.88
Holocellulose	77.5 ± 2	6.58
Extractives soluble in alcohol - acetone	12.2 ± 0.1	4.54
1% NaOH solubility	50.3 ± 1.6	4.31
Ash	6	0

Table 2. Fiber dimensions and morphological coefficients of rapeseed residues.

Fiber dimension	Value %	Coefficient of Variation %
Length	1.190 ± 0.2 (mm)	23.3
Width	32 ± 6 (µm)	18.9
Cell wall thickness	4 ± 2 (µm)	36.16
Felting coefficient	37.14	
Runkel coefficient	0.44	
Flexibility coefficient	69	

Table 3. Different yields of rapeseed NSSC pulps (Constant pulping temperature: 175 °C).

Pulping variable		Digester yield (%)	Defibration Yield (%)		
Active* alkali (%)	Pulping time (min)		Reject	Screened	Total
8	20	87^{l**}	5	67	72^{h**}
10		86^{l}	4.5	67	71.5^{h}
12		83.6^{k}	3	66	69^{g}
14		83^{k}	2.5	66	68.5^{fg}
16		81^{j}	2	65	67^{ef}
8	40	74^{i}	1.5	64	65.5^{f}
10		70^{h}	1.5	62	63.5^{d}
12		66^{g}	1.5	62	63.5^{d}
14		65^{fg}	1	61	62^{d}
16		64^{ef}	0.9	61	61.9^{d}
8	60	63de	0.9	59	59.9^{c}
10		62^{cd}	0.8	58	58.8^{c}
12		60.5^{bc}	0.7	58	58.7^{c}
14		60^{ab}	0.7	56	56.7^{b}
16		58.5^{a}	0.5	54	54.5^{d}

* Based on NaOH
** Superscript letters in the table indicate statistically significant difference and Duncan ranking of the average value of measured property

handsheet strength and optical properties and the kappa number of the pulps are summarized in Table 4. The kappa number of these pulps varied between highest value of 66 to the lowest value of 45 and the influence of pulping time showed more effective than chemical charge on kappa number. Tear index, breaking length, burst index, and tensile index of pulps were measured. Even though the influence of chemical charge on strength indices revealed that higher chemical charges improve strength values of the pulps, the effect of pulping duration is more effective and as pulping duration increases from 20 min to 40 and 60 min, tear index, breaking length, burst index, and tensile index increases to 7.5 $mN.m^2g^{-1}$, 6.78 km, 2.57 $kPa.m^2g^{-1}$ and 66.5 $N.mg^{-1}$, respectively. However, brightness reduced to 21% ISO and opacity improved to 99.9% ISO. The results of the statistical analysis showed that chemical charge significantly influenced both strength and optical properties. The Duncan ranking of the average values of strength and optical properties measurement is shown in Table 4.

Discussion

The length of the fibers (1.19 mm) from rapeseed residue is in the range of hardwoods and other agricultural residues, such as bagasse (1.13 mm) (Sanjuan et al. 2001), and shorter than wheat straw (1.73 mm) (Mackean and Jacobs 1997) and 1.5 mm (Mohan et al. 1988), and date palm tree rachis fibers (1.3 mm) (Khristov et al. 2005). Runkel coefficient of rapeseed residue is less than both wheat straw (0.67) and bagasse (0.67) as well as date palm rachis (0.8) and leaves (0.9) (Khristova et al. 2005), but the flexibility coefficient of rapeseed stem fibers is higher than either date palm rachis and leaves and bagasse (Sanjuan et al. 2001). This indicates good sheet formation potential of these fibers. However, the felting coefficient is not as good as date palm residues.

Both cellulose and lignin content of this material is low compared to softwood and hardwoods. However, it is higher than most of the agricultural residues (Sanjuan et al. 2001; Mackean and Jacobs 1997). Our in house observation shows very interesting behavior

Table 4. Properties of selected NSSC pulps from rapeseed residues.

Trail code	Active alkali (%)	Pulping time	Total yield (%)	Kappa No.	Caliper (µm)	Tear index ($mN.m^2g^{-1}$)	Tensile index ($N.mg^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2g^{-1}$)	Brightness (%)	Opacity (%)
A_1	8	20	72	66	205	6^{a}	35.6^{a*}	3.63	1.7^{a}	41.2^{a}	97.2^{ab}
A_2	10		71.5	65	200	6.2^{ab}	38.2^{b}	3.89	1.75^{a}	39.1^{a}	98.2^{c}
A_3	12		69	64.5	195	6.4^{bc}	39.2^{b}	3.99	1.87^{ab}	40.2^{a}	97.6^{bc}
A_4	14		68.5	63.5	185	6.6^{cd}	42^{c}	4.28	2.03^{b}	42.3^{a}	96.6^{a}
A_5	16		67	56.5	180	6.9^{d}	44^{d}	4.48	2.04^{b}	43^{a}	97^{ab}
B	12	40	63.5	50	140	7.4	57.8	5.89	2.46	22.6	99.2
C		60	58.7	45	130	7.5	66.5	6.78	2.57	21	99.9

* Superscript letters in the table indicate statistically significant difference and Duncan ranking of the average value of measured property

of rapeseed lignin. Under different chemical treatments, we have observed varying color changes from red under soda treatment to dark brown under alkaline sulfite. However, upon exposure to a mixture of sodium sulfite and sodium hydroxide and mild temperature, a light color appeared.

The performance of rapeseed residues in different pulping processes, such as soda and NSSC pulping, varies considerably and usually a low yield is observed. Even though it was possible to reach defibration yield between the lowest value of 54.5% and the highest value of 72% (digester yield between 58.5%-87%), but reaching a high yield is difficult with this material. The yield of soda-AQ pulping of rapeseed residue was measured as 36.8% (kappa number of 24) (Mousavi et al. 2009) and for soda as 36.1% at kappa number of 17 (Molaie, unpublished data). Ates et al. (2008) reported screened yield of between 42.9% (Formacell process) and 48.2% (low alkali kraft-AQ) and a reject between 1.4% and 3.6% for similar pulps produced from wheat straw. The yield of other pulping processes such as high alkali kraft-AQ, soda-AQ, Alcell, and Bio-kraft varied between these numbers. The higher reject in our experiment may be attributed to the size of the refiner. A single disc refiner equipped with 25 centimeter disc was used and since the total weight of the pulping sample was low, then the remaining material inside the refiner was higher than using a pulp disintegrator, which causes a higher reject. It can be concluded that with careful refining and back water circulation, defibration yield can be improved.

Since the objective of this study was the production of suitable pulp for unbleached paper production or utilization of the pulp as substitute for recovered brown stock, the higher yield pulps were selected for further evaluation. The selected pulp yields and kappa numbers are shown in Table 4. Pulps were refined to 375 ± 5 mL CSF and handsheets were made. The results show that at higher alkali charge or pulping duration, pulp strength improved, and the influence of pulping duration is more effective than alkali charge. Changing the alkali charge from 8% to 16% increases the tear index from 6 to 6.9 mN m^2g^{-1}, breaking length from 3.63 to 4.48 km, burst index from 1.7 to 2.04 kPa m^2g^{-1}, and tensile index from 35.6 to 44 N mg^{-1}. Brightness was improved from 41.2% ISO to 43% ISO and opacity remained almost constant at about 97%. However, upon extending the pulping time from 20 min to 60 min, strengths, especially the tensile index, considerably increased. Even though, the tensile and burst indices of rapeseed residue NSSC pulp is lower than wheat straw kraft pulps (89.15 ± 3 Nmg^{-1} and 3.32 ± kPa m^2g^{-1}), its tear index is almost identical (Ates et al. 2008). However, at a similar freeness, the strength of pulps from date palm residues is higher (Khristova et al. 2005). The relation between tensile and tear strength (Figure 1) shows that tensile and tear strength increase simultaneously. Since the strength of either soda or soda/AQ pulps from rapeseed residue are lower than NSSC, it can be concluded that rapeseed residues is suitable for unbleached NSSC pulp production.

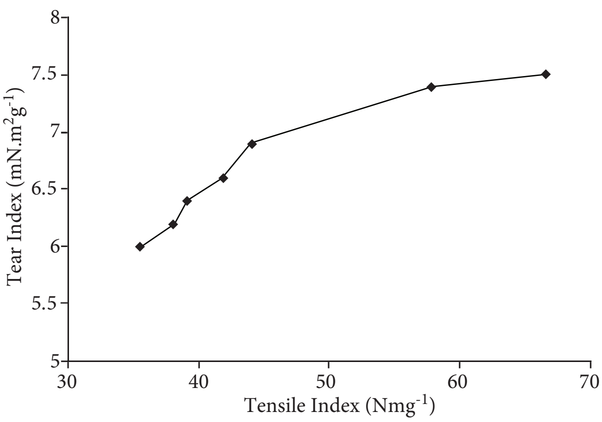

Figure 1. The relationship between tensile and tear strength of the NSSC pulp from rapeseed residues.

Conclusion

Under the pressure of environmentalists, world paper industry has been searching for alternative raw materials for future fiber supply and the situation in fiber deficient countries, especially in the Middle East, is so severe that these countries can not develop their national paper industry. Even though Iran is fortunate to possess a good supply of bagasse, but it still must look for other fiber supplies to fulfill its fiber requirement. Therefore, different research groups have been looking at different fiber resources including wheat straw, sunflower stalks, and corn stalks as well as rapeseed residue as investigated in this study. Fiber dimension and chemical composition of rapeseed residue is measured. Then NSSC pulping trials were performed applying different chemical charges and pulping times. The results indicated that rapeseed residues are suitable for NSSC pulping and application of 12% active alkali, 60 min pulping time at 175 °C pulping temperature will produce pulp suitable as supplement pulp for unbleached paper production. Tensile index, breaking length, burst index, and tear index of this pulp (58.7% total yield) were measured as 66.5 N mg^{-1}, 6.78 km, 2.57 kPa m^2g^{-1}, and 7.5 mN m^2g^{-1}. Pulping this raw material will allow the utilization of this unused material.

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