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RAPESEED STALKS FOR PAPERMAKING: STUDIES ON PULPING, REFINING AND DEWATERING

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Cereal straw, bamboo and bagasse are the most widely used non-wood raw materials, but work is being done towards other interesting sources of fibres, such as rapeseed stalks and straw. Rapeseed oil production for energetic purposes is increasing, and so are wastes. In this work, pulps from *Brassica napus* (rapeseed) stalks were obtained by soda-anthraquinone and Organosolv cooking. They were refined in a PFI mill. Handsheets made from those pulps were tested. Drainage rate and retention of fillers were also evaluated. We address the capabilities of rapeseed stalks and stems for papermaking and the influence of refining on the mechanical properties, the morphology of fibres and the amount of fines. This material was found to be suitable for papermaking and, as an advantage, a small number of PFI revolutions resulted in a substantial gain in mechanical properties.

Keywords: rapeseed, soda-anthraquinone, organosolv pulping, paper properties, drainage

INTRODUCTION

The manufacturing of paper from non-woody plants works in three ways to diminish the environmental impact. First, by re-using residues their open burning is avoided, a hazardous activity that causes air pollution. Second, the pulping of non-wood materials gives satisfying results using sulphur-free methods, such as SAICA's semichemical process cooking.[1] Finally, their processing may result in energy savings, as many non-wood species need less energy consumption in the refining process, or may not even require refining at all.[2]

The European Union (EU) is the largest rapeseed (*Brassica napus*) producer in the world, as the Union members produce 21.1 million tonnes annually, out of a worldwide production of 60 million tonnes. Still, the EU is also the greatest consumer, as 2.2 million tonnes are imported annually and only 0.1 million tonnes are exported.[3] Rapeseed main products are oil, used as a lubricant in industrial applications and for human consumption, and meal for animal feeding.

Rapeseed oil is being used and studied as an interesting source for biodiesel production,[4] and as a source of polyacids to manufacture biocomposites.[5]

The potential of rapeseed wastes for papermaking has already been studied by Mousavi *et al.*,[6] as they analysed rapeseed straw and its papermaking potential. Soda-anthraquinone pulping showed better results than soda alone. Tofanica *et al.*[7] characterised rapeseed stalk fibres, and found them to be very slender, with length ranging from 0.71 to 1.99 mm, and width from 9.10 to 19.60 μm. Potůček *et al.*[8] found that rapeseed stalks are mainly constituted by holocellulose (76.15%) and lignin (21.35%). According to them, paper from rapeseed straw pulp has a higher breaking length than paper from many other non-wood materials.

The ancient soda pulping method was relegated in benefit of the kraft process, but the addition of anthraquinone as a homogenous catalyst has made it a competitive technique, and it seems to be especially competitive for annual plants.[9,10,11] Another unconventional method, organosolv pulping, implies the use of organic solvents, such as methanol or ethanolamine. Despite its higher energy consumption, it allows for lignin recovery and higher yield values than the soda-anthraquinoneprocess.[12,13]

A weakness of the pulps made from many non-wood materials to be used for papermaking is their drainage behaviour. Compared to pulps from wood materials, drainage time is notably longer. This could be explained by their high content of parenchyma cells.[14] The use of adequate retention agents is necessary to increase the retention of fillers and the dewatering rate.

In this work, chemical pulps from *Brassica napus* stalks were obtained through minimal environmental impact techniques (soda-anthraquinone cooking and organosolv cooking), refined and tested for their papermaking potential. Tests involved the preparation of paper sheets, their mechanical characterization and the study of their drainage properties. This work aims to evaluate the potential application of rapeseed stalks for papermaking purposes, and to discuss the influence of cooking conditions and refining.

EXPERIMENTAL

Materials

Specimens of rapeseed (*Brassica napus*) were grown in Castilla y León, Spain, and stalks or stems of all diameters were harvested as raw materials for pulping.

Sodium hydroxide pellets and a monoethanolamine commercial solution were provided by Panreac, as were ammonia, solid ammonium chloride and ethylenediaminetetraacetic acid (EDTA). Anthraquinone was purchased in powder form from Sigma Aldrich. As filler, we used precipitated calcium carbonate (PCC) for analysis from Merck, with an approximate particle size (d_{50}) of 14 µm.

Two linear polyelectrolyte-based flocculants (retention agents) were supplied by Nalco Chemical Company. One of them was a co-polymer of acrylamide of high molecular weight with cationic charge, hereinafter referred as "cationic flocculant". The other one was a co-polymer of acrylamide of medium molecular weight with anionic charge, referred from now on as "anionic flocculant". Solutions of polyelectrolytes were prepared by adding 0.3 g of dry flocculant to 300 mL of water. The furnish was kept under gentle stirring (120 rpm) for 90 minutes.

Pulping

Stalks were isolated, crushed, and introduced into a stainless steel batch digester. Cooking took place by using ethanolamine (organosolv pulping) and sodium hydroxide. For the latter, anthraquinone was added to increase the selectivity towards lignin. Conditions are summarized in Table 1. Liquor-to-solid ratio was held at 6. Temperature was kept constant by means of a PID controller. The resulting pulps were washed, screened and stored at 4 °C. Remaining lignin was analysed following TAPPI Useful Method 246, Micro-Kappa number, given that the amount of sample was limited.

Refining

Prior to refining, the pulps were disintegrated by means of a lab disintegrator ENJO model 692 according to ISO 5263, working at 3000 rpm. Pulp refining was carried out by a Maskin's Mark VI PFI mill at 10% consistency in accordance with ISO 5264/2. The power of the engine was 0.37 kW and the voltage applied was 220 V. Three refining intensities were used: 250, 500 and 1000 PFI revolutions.

The refining degree of the unbeaten and beaten pulps was measured using a Canadian Standard Freeness (CSF) tester, following the TAPPI standard T227 om-94. Up to four replicates were made, and in each case the relative standard deviation was not higher than 3%.

Morphological characterisation

A morphological analyzer (MorFi) from Techpap was used to determine the dimensions of fibers (length and width), the fibre population and the amount of fines in each pulp sample. Both unrefined and refined pulps were subjected to this characterisation, which is based on an image analysis system. Fines were defined as those fibrous particles whose length ranged from 10 µm to 90 µm. The proportion of fines was expressed as the average percentage of the area occupied by fines in the images taken. The suspensions were prepared by dispersing 2 grams of pulp (oven-dry weight) in 1200 mL of water. Three replicates were made for each of the pulp samples.

Handsheet preparation and testing

Ten handsheets, with an oven-dry weight of 60 g/m^2, were obtained from each of the pulps according to the ISO 5269-1:1998 standard. The experimental equipment consisted of a pulp dispersing-disintegrator, conventional sheet former, press (130 kPa), and heating system to remove moisture. Agitation was done by hand, by means of a standard stirrer. Blotters and standard couch weights were used to separate the wet sheet.

Brightness was determined according to ISO 2470-1:2009. The tensile index of the handsheets was measured by means of a mechanical tester from HT Hounsfield following the ISO 1924-2:2009 standard. Tear index was determined by a MESSMER tester according to UNE-EN 21974:1996. To measure burst strength, a METROTEC tester was used and the ISO 2758:2004 standard was followed.

Table 1
Pulping conditions and properties

Pulp code	Reagent	T (ºC)	t (min)	Yield (%)	Kappa no.	ISO brightness (%)
ETN40	40% ethanolamine, 60% water	140	40	77.6	46.4	38.9
ETN60	60% ethanolamine, 40% water	180	60	58.7	30.9	39.7
SAQ10	10% NaOH, 0.1% AQ on o.d. pulp*	140	40	69	48.1	37.5
SAQ20	20% NaOH, 0.1% AQ on o.d. pulp*	180	60	54.5	29	40.8

*On the basis of oven-dried pulp weight
T: cooking temperature; t: cooking time; ETN: ethanolamine; S: soda; AQ: anthraquinone

Drainage testing

In order to test the drainage performance, a lab device DFR-05 from Mütek was used. Only the pulp coded SAQ10 (Table 1) was tested, since the drainage behaviour is more dependent on the nature of the raw material, the size, shape and content of the filler and the refining degree than on the cooking method. A pulp suspension at 0.5% consistency was prepared with tap water of conductivity 500 µS/cm. This suspension was mixed with calcium carbonate (filler). The total mass of the suspension was 500 grams. We used 0.16 grams of filler per gram of dry pulp. The pH of the suspension was adjusted to 7 by adding small amounts of HCl.

The mixture was put into the stirring chamber. The “Drainage” program was selected in Mütek’s software. We set the stirring at 200 rpm for 60 seconds. Then a retention agent was added into the suspension, and we ran the stirrer for 30 seconds more at 300 rpm. The suspension went through a 100 mesh screen, wire size being 0.11 mm. The cake was rejected and the filtrate was collected for analysis.

The amount of precipitated calcium carbonate in the filtrate was determined by complexometric titration with EDTA. Eriochrome Black T was used as indicator. A buffer solution of ammonia and ammonium chloride was used to keep the pH around 10. Knowing the amount of filler in the filtrate and in the initial furnish, the amount of filler retained in the fibrous matrix was determined by difference. As tap water was used, we also measured its hardness, following this same method, to apply a correction.

The drainage tests performed on Mütek’s device were repeated on the handsheet formation apparatus, in order to confirm the results or point out the differences found. Again, a pulp suspension of 0.5% consistency and tap water were used. The total mass was 4 kg and the pH, slightly above 7, was not adjusted. The nominal aperture size of the wire screen was 0.125 µm (115 mesh). A fourth part of each of the handsheets was disintegrated and dispersed in water. The amount of calcium carbonate in this suspension was determined by titration with EDTA. This was a direct measurement of the amount of PCC retained in the handsheets.

RESULTS AND DISCUSSION

Besides the conditions under which stalks were cooked, Table 1 shows the yield obtained, expressed as the weight of oven dried pulp obtained per weight of oven dried stalks. The Kappa number and ISO brightness are also shown.

Table 2 shows the mechanical properties of the handsheets for the different beating degrees. The deviations are expressed for a confidence level of 90%. Fibre length and coarseness are shown in Table 3, along with the number of fibres per gram of oven-dry pulp and the proportion of fines.

Table 2
Influence of cooking and refining on the mechanical properties

Pulp	PFI revolutions	Tear index (mN m^2/g)	Burst index (kN/g)	Tensile index (N m/g)
ETN40	0	11.1 ± 0.7	0.84 ± 0.04	7.5 ± 0.1
	250	13.3 ± 0.4	0.97 ± 0.06	14.2 ± 0.6
	500	15.0 ± 1.0	1.45 ± 0.05	16.2 ± 0.4
	1000	17.6 ± 0.3	1.87 ± 0.14	18.1 ± 0.9
ETN60	0	11.5 ± 0.3	0.84 ± 0.05	10.2 ± 0.5
	250	13.9 ± 0.5	1.53 ± 0.11	22.9 ± 2.0
	500	14.2 ± 0.4	4.87 ± 0.30	45.8 ± 1.8
	1000	15.2 ± 0.7	5.14 ± 0.26	47.5 ± 3.1

SAQ10	0	4.6 ± 1.0	0.73 ± 0.08	8.2 ± 0.3
	250	12.6 ± 0.9	1.25 ± 0.12	12.9 ± 1.1
	500	17.8 ± 0.5	1.52 ± 0.04	17.2 ± 0.5
	1000	19.9 ± 0.6	2.18 ± 0.11	26.6 ± 1.5
SAQ20	0	14.0 ± 1.2	0.72 ± 0.04	9.5 ± 1.0
	250	20.1 ± 0.8	1.62 ± 0.11	17.1 ± 0.4
	500	21.8 ± 0.9	2.12 ± 0.06	19.8 ± 1.1
	1000	19.5 ± 0.5	3.70 ± 0.19	38.5 ± 1.7

Table 3
Influence of cooking and refining on the characteristics of fibres, their population and the number of fines

Pulp	PFI revolutions	Average length (μm)	Coarseness (mg/m)	Number of fibres (10^6 g^{-1})	Proportion of fines (% in area)
ETN40	0	617	0.201	13.7	7.20
	250	567	0.162	18.0	8.37
	500	582	0.147	19.3	9.60
	1000	554	0.139	21.1	10.06
ETN60	0	574	0.106	27.3	7.74
	250	543	0.116	25.3	8.95
	500	563	0.114	25.4	9.05
	1000	507	0.115	26.2	9.34
SAQ10	0	654	0.166	16.6	4.51
	250	629	0.114	24.0	5.41
	500	628	0.108	25.5	6.00
	1000	617	0.095	28.7	7.01
SAQ20	0	632	0.114	15.9	4.40
	250	632	0.085	31.6	4.56
	500	621	0.082	32.9	4.92
	1000	587	0.083	33.2	7.03

Influence of cooking conditions

Mild treatments, at 140 ºC and after 40 minutes of cooking, resulted in higher yields, more pronounced for the organosolv pulps. However, only severe cooking provided enough removal of lignin to make feasibly bleachable pulps, as it achieved Kappa numbers around 30.

Unbleached pulps from rapeseed stalks showed good values of brightness (around 40%), even when cooked under mild conditions. ISO brightness of rapeseed straw pulps, according to the experiments of Mousavi *et al.*,[6] lies around 16-18%. Unbleached rice straw kraft pulps, Alfa soda pulps and *Eucalyptus citridiora* kraft pulps show brightness values of 45-50%,[15] 47%,[16] and 15-20%,[17] respectively. Hence, the brightness values of the pulps studied are in the high range.

Cooking under severe conditions gave higher burst index and tensile index (Table 2). These values were found to be particularly high for the organosolv pulps. Also, severe conditions caused fibre coarseness to decrease (Table 3), which has a positive effect on fibre bonding.[18] Cooking with ethanolamine resulted in the largest amounts of primary fines (i.e., before refining). This is likely due to the lesser damage to carbohydrates. Therefore, the proportion of fines in organosolv pulps ranges between that of mechanical pulps and that of soda pulps.

Influence of refining

Figure 1 presents the degree of refining, expressed as Canadian Standard Freeness, for the different pulps. For all pulps, 1000 PFI revolutions were enough to achieve freeness values below 350 mL. Hardwood kraft pulps need around 3000 PFI revolutions to get to such a low refining degree, and softwood kraft pulps need more than 5000 PFI revolutions.[19] Therefore, the use of rapeseed stalks implies great energetic savings at this stage, as expected from a non-wood material.[2] Pulp ETN60 showed the lowest freeness values, since the freeness of the pulp was already low prior to refining, meaning that Organosolv pulping alone resulted in good fibre-to-fibre bonding.

The tear index values of the sheets from non-refined pulps were high enough for papermaking, while the tensile index and the burst index were still too low for that purpose (Table 2). Hence, a refining stage would be necessary to obtain pulps of sufficient quality.

The tear index was slightly improved by refining (Table 2) and was in the high range, similar to that of soda pulps from abaca.[20] The tensile and burst indices were greatly increased from non-refined pulps to 1000 PFI revolutions, the burst index being similar to that of rice straw pulps.[15]

As expected, fibre length decreased with refining (Table 3), but this shortening was not a major drawback considering that 500 PFI revolutions may be enough to produce printing paper. Coarseness was found to decrease notably from 0 to 250 PFI revolutions and hardly changed with further refining, whereas fibre population showed the opposite trend. Refining resulted in a great generation of fines, considering the low numbers of PFI revolutions. This is related to the abrupt decrease in freeness.

Drainage properties

Low freeness is associated with slow dewatering and compels manufacturers to use a longer paper machine or to decrease the production rate.[14,21] In addition, a great amount of energy is consumed by drying. In this work, water removal was not increased, but the use of flocculants could hasten it.

The more retention agent was added to the chamber, in the range that was studied, the faster the drainage was, as shown in Figure 2. This does not imply that the process could be improved by using even higher dosages of retention agent. A small addition of cationic flocculant was enough to achieve a great reduction of the time at which an asymptotic value of the filtrate weight was reached, while further additions gave a slight improvement (Figure 2B). As for the anionic flocculant, a concentration of 6 mg/L was needed to get the drainage time obtained for 3 mg/L of cationic flocculant.

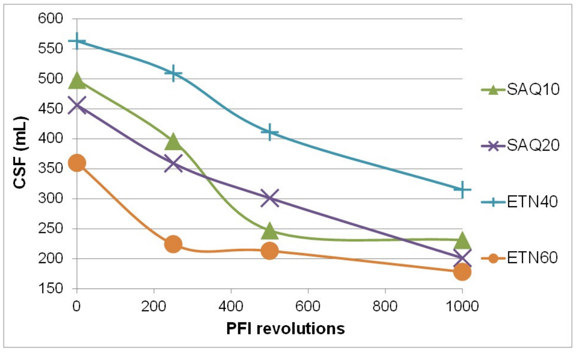

Figure 1: Evolution of Canadian Standard Freeness with the number of PFI revolutions

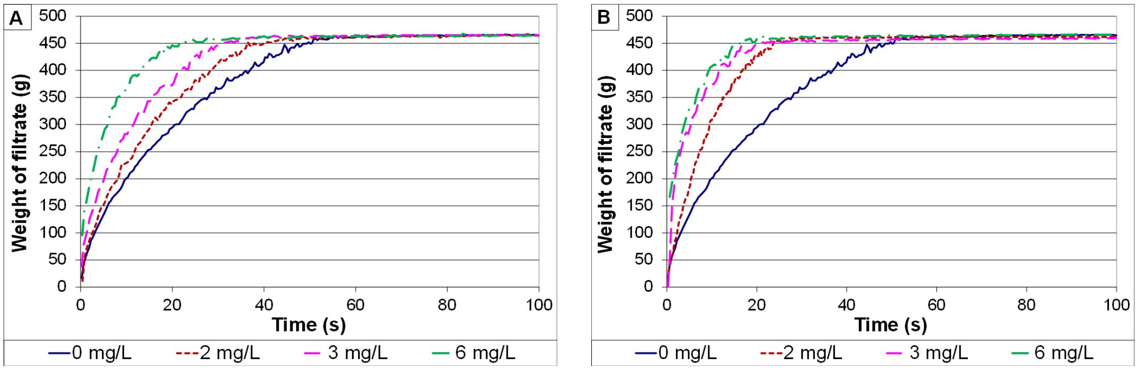

Figure 2: Drainage – weight versus time curves for different amounts of added anionic flocculant (A) and cationic flocculant (B)

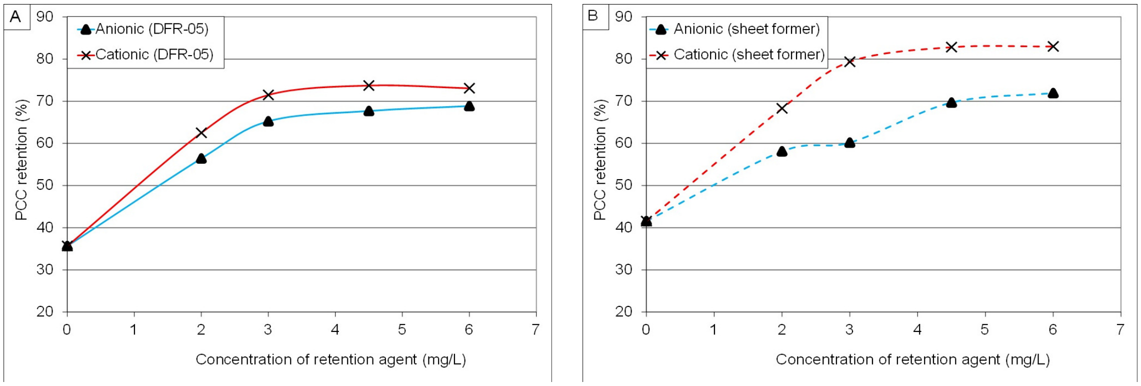

Figure 3: Evolution of filler retention with the concentration of anionic and cationic flocculants, using the DFR-05 (A) or the handsheet formation apparatus (B)

Figure 3A shows the evolution of filler retention in the pulp with the amount of retention agent added, when Mütek's device was used. Both flocculants made calcium carbonate retention reach values around 70%. Concentrations higher than 6 mg/L were not considered, since the curves tend to reach an asymptotic value (anionic flocculant) or a maximum peak (cationic flocculant).

As shown in Figure 3B, when using the handsheet former, the initial retention of PCC (without retention agents) was higher. This was due to the lower aperture size of its wire screen. Upon addition of the cationic flocculant, the retention reached 83%. Nonetheless, the proportional increase was slightly lower since stirring was done by hand. Agitation influences the adsorption of polyelectrolytes on fibres and fines, and thus the kinetics of flocculation. The advantage of the cationic flocculant over the anionic one was confirmed and it became more evident without automatic stirring.

It may be concluded that a cationic polyacrylamide is better for drainage and retention of calcium carbonate, as expected.[22] This is explained by the presence of dissociated carboxyl groups, negatively charged, in pulp fibres.

CONCLUSION

Comparing the brightness and mechanical properties of pulps from rapeseed stalks with those of pulps from rapeseed straw, rice straw and common hardwoods, it can be concluded that rapeseed stalks represent a source of fibres suitable for producing market pulp and/or certain grades of paper. Handsheets prepared from the pulps that were studied showed high tear index and their brightness was found to be in the high range. The mechanical properties were notoriously improved by refining. Even low numbers of PFI revolutions resulted in the generation of large amounts of fines and in a strong decrease in fibre coarseness.

Organosolv pulping under severe conditions is recommended, since low freeness values are achieved with little refining energy consumption. Moreover, it results in the highest mechanical resistance.

The retention of calcium carbonate in a non-refined pulp sample was clearly improved by the addition of polyelectrolyte-based flocculants, the cationic polyacrylamide being the best. The dewatering rate was also increased. When the consistency of the suspension is 0.5%, a dosage of 3 mg of cationic polyacrylamide per liter of water is suggested.

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