RAPESEED STRAW AS AN ALTERNATIVE FOR PULPING AND PAPERMAKING

IRYNA DEYKUN,[*] VITA HALYSH[*,**] and VALERII BARBASH[*]

[*]*Department of Ecology and Plant Polymers Technology, Igor Sikorsky Kyiv Polytechnic Institute, 37/4, Peremogy Av., Kyiv 03056, Ukraine*
[**]*Department of Physico-Chemistry of Carbon Materials, O.O. Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17, General Naumov Str., Kyiv 03164, Ukraine*
✉ *Corresponding author: Valerii Barbash, v.barbash@kpi.ua*

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Nowadays, it is necessary to develop new native resources of raw materials for producing consumer goods, in particular, pulp and paper, because of the increased demand for pulp for papermaking and the shortage of wood. In this study, rapeseed straw was studied in order to evaluate it as pulping raw material. Laboratory experiments were carried out to investigate the effect of cooking parameters on the properties of rape pulp. The obtained results indicate that the cooking conditions have an impact on pulp yield, residual lignin content and brightness. The fibre length distribution, as well as the physical properties of handmade paper sheets, was investigated. Comparing the results obtained, it can be concluded that the peracetic pulp obtained with sodium molybdate catalyst presents better results with regard to strength properties. The possibility of using organosolv rape pulp in the composition of printing paper was evaluated. In conclusion, rape straw can be recommended for peracetic pulp and paper production.

Keywords: rapeseed straw, non-wood, peracetic acid, pulping, paper sheet, physical properties

INTRODUCTION

The most common initial material for papermaking is represented by wood fibers. The exploitation of forest resources to produce pulp has increased rapidly. At the same time, other industries, such as furniture production, building and others, need the same type of raw material.[1,2] On the other hand, global deforestation creates ecological problems and climatic changes. Therefore, alternatives must be found.

Non-wood plant raw materials offer an opportunity to decrease the use of wood for the papermaking industry. Plant raw materials from 'on-purpose' or dedicated crops (jute, hemp, miscanthus, bamboo), naturally occurring uncultivated crops (grasses, reed), agricultural residues (wheat straw, rice straw, corn stalks, sugarcane bagasse, canola, banana stem), can be an alternative source of cellulose for papermaking.[3-14]

Rapeseed straw, a large-scale waste product of agro-industrial processing, occupies an essential place in the total amount of the agricultural wastes in many countries. This residue is used in small quantities as organic compost. However, most of it is left in the fields, causing risk of fire and air pollution. Rape stalks are composed of three main constituents, namely, lignin, cellulose and hemicelluloses, and can be used for obtaining pulp that will help to decrease or replace the use of wood fibers in papermaking.[15,16]

There are relatively few standard methods to obtain pulp from wood and non-wood plant raw materials. These include are the soda, sulfate, sulfite and neutral-sulphite methods, which negatively influence the environment because of the application of sulfur-containing reagents for lignin removal from plant materials. Most of the lignin is removed during pulping, while some residual lignin can be removed during the additional stage by bleaching using chlorine-based and oxygen-based chemicals.[17,18]

Organosolv delignification has been suggested as an environmentally friendly process and an alternative way for obtaining pulp. Organic reagents have potential to remove lignin and hemicelluloses at boiling temperature.[19,20] A

variety of organic solvents, such as esters, alcohols, glycols, ketones and organic acids, have been proposed for pulping.[21]

Among organic solvents, acetic acid can be regarded as a potential agent to achieve extensive delignification due to its relatively low cost. The application of hydrogen peroxide during pulping promotes the delignification of raw materials; increased brightness can be also achieved by delignification with peroxy compounds. At the same time, a less pronounced impact on cellulose is observed during pulping with such compounds.[22] The cooking process is carried out at low temperature, which involves low energy consumption. The use of catalysts, such as inorganic acids and salts, can help to improve the quality of the pulp.[23,24] The disadvantages of inorganic acid catalysts consist in their corrosion activity and their ability to accelerate the hydrolysis reactions of polysaccharides. The most active and effective catalysts for delignification are molybdenum and tungsten acids, as well as their salts.

Our previous studies have characterized the rape pulp obtained with peracetic acid at different solid/liquid ratios, temperature, during different time and the results indicated that peracetic pulp has low content of lignin and high brightness.[25] The use of sodium tungstate and sodium molybdate allows improving the pulp yield and lignin content. However, the morphological and papermaking properties of such pulps must be studied.

The aim of this study was to obtain pulp from rapeseed straw, using catalytic peracetic treatment, and to investigate its morphological, physical and mechanical properties, as well as the possibility of using it to produce one of the most common types of paper.

EXPERIMENTAL

Materials

Rapeseed straw was obtained from the Poltavskiy region of Ukraine. The straw was sorted out of leaves and pods, ground, sieved, crushed to the size of 15-20 mm, stored in desiccators for maintaining a constant moisture level, and used for further investigations. The chemical composition of the rapeseed straw was determined in accordance with existing TAPPI standards, namely: T222 cm-02 for lignin, T207 cm-99 for substances extracted with hot water, T 212 cm-02 for substances extracted with 1% solution of NaOH, T204 cm-97 for substances extracted with ethanol-benzene solution, T211 om-02 for ash content.[26-30] The cellulose content was determined following the Kurschner-Hoffer method.[31] The content of the main components in the raw material was as follows: cellulose – 37.7%; pentosans – 29.6%; lignin – 26.4%; ethanol-benzene extractables – 3.6%, hot-water solubles – 10.1%; 1% NaOH solubles – 24.2%; ash – 0.05%.

Peracetic acid preparation

The solution of peracetic acid was used as cooking liquor and was made by mixing ice acetic acid and 30 wt% hydrogen peroxide at the volumetric ratio of 70:30%. The cooking solution was kept for a few days in a dark cupboard to achieve the concentration of peracetic acid of 11 wt%. The resulting solution was subsequently diluted with distilled water to reduce the peracetic acid concentration to the desired values and used in the cooking process.

Cooking process

Glass flasks with a volume 1 dm^3 were loaded with 20 g of rapeseed straw. Cooking liquor was then added; the ratio of liquids to solids was 9:1. Sodium tungstate and sodium molybdate of 0.1% on oven-dry raw material were used as catalysts and were added to the cooking mixture. The flasks were placed in a water bath and heated to 95 °C during 90-180 min. To ensure the cooking process and to eliminate the loss of the cooking liquor, the flasks were connected to a reflux setup. After reaching the cooking time, the flasks were removed and cooled under a stream of cold water, the spent liquors were separated and the pulp was washed with distilled water to achieve a neutral medium. The pulp was then dehydrated and dried in the air to constant moisture content of 5-7%.

Preparation of pulp handsheets

The rape pulp was beaten in a Valley beater at 6% consistency to 60 ^oSR. The handsheets of peracetic rape pulp of 75 ± 1 g m^{-2} were formed on a Rapid-Kothen unit.

Preparation of paper handsheets

The obtained peracetic rape and bleached Kraft pine pulps were beaten separately in a Valley beater at 6% consistency to 35 ^oSR. The effect of the ratio between peracetic pulp and kraft pulp on the strength efficiency of paper was studied. A series of five kraft pulp contents (0, 25, 50, 75 and 100%) was examined. Paper handsheets with an average weight of 75 g m^{-2} were produced in combination with cationic starch to increase the strength of the sheet and with kaolin as retention agent to increase the printing and written capacity. The consumption of starch and kaolin was 3% and 15%, respectively.

Analysis

The pulp yield was determined gravimetrically. The Klason lignin and Kappa number of the pulp was

determined in accordance with T222 om-02 and T236 om-99.[32]

Fiber length distribution of the pulp samples was estimated using an FS-100 system (Kajaani Electronics Ltd.). A stock suspension of fibers with 0.01% consistency was prepared and used for investigation.

The handsheets were conditioned at 20 °C, 65% relative humidity during 24 h. The pulp handsheets were characterized as to their physical properties following T220 sp-01 (TAPPI, 2001). The breaking length and tear index of the paper sheets were characterized according to T494 om-01 (TAPPI, 2006), while brightness – in accordance with T525 om-92 (TAPPI, 1992).[33-35]

RESULTS AND DISCUSSION

Effect of cooking conditions on pulp properties

To evaluate the effect of the catalyst type and the duration of cooking on the properties of the rape pulp, the cooking was held at a constant liquor ratio of 9:1, pulping temperature of 95 ± 1 °C and catalyst consumption of 0.1%. The total pulp yield, residual lignin content and brightness of the obtained pulps were determined and the results are presented in Table 1.

The data of Table 1 show that increasing the cooking time from 90 to 180 min, in the absence of the catalyst, decreases the rape pulp yield from 53.0 to 41.8% because of the increased dissolution of lignin, extractive substances, mineral components and maybe some degraded polysaccharides. A decrease in kappa number from 9.9 to 4.0 during cooking increases the brightness of the pulp from 78.3 to 83.1%. The brightness of the obtained peracetic rape pulps reached high values, in comparison with those of bleached pulps from other annual plants. For example, the brightness of bleached soda-anthraquinone rice straw pulp reaches 82.2% and the bleached chemimechenical pulp from wheat straw has a brightness value of 61.2%.[36,37]

As can be seen from the obtained data, the use of the investigated catalysts leads to a decrease in the content of lignin and in the yield of pulp, compared to non-catalytic cooking. According to the results, minimal residual Klason lignin in the rape pulp is obtained when using Na_2MoO_4 as catalyst.

The effect of peracetic acid concentration in the cooking liquid and the catalyst type on the properties of the rape pulp is illustrated in Figure 1. The obtained data indicate that increasing the peracetic acid concentration from 3.5 to 11.0 wt%, in all the cases, decreases the pulp yield (Fig. 1a). A significant decrease in pulp yield, with an increase in peracetic acid concentration in the cooking solution, is associated with the oxidation of lignin, accelerating the reactions of oxidative transformation of polysaccharides into soluble low molecular weight products. At the same time, the brightness (Fig. 1d) of the pulp increases due to delignification of the plant raw material (Fig. 1b, c).

Table 1
Cooking conditions and properties of rape pulp

Catalyst	Time (min)	Pulp yield (%)	Klason lignin (%)	Kappa number	Brightness (%)
Without	90	53.0	2.8	9.9	78.3
	120	46.8	2.1	8.6	81.6
	180	41.8	1.4	4.4	83.1
Na_2WO_4	90	45.3	2.0	8.7	77.7
	120	42.5	1.6	7.1	80.6
	180	41.0	1.1	5.5	82.8
Na_2MoO_4	90	47.3	1.8	8.5	76.5
	120	45.5	1.4	4.5	79.3
	180	41.3	0.8	4.0	82.5

The comparison of the impact of various catalysts indicates that sodium molybdate shows better activity in the delignification process of rape straw with the peracetic acid solution. The pulp obtained with the use of sodium molybdate is characterized by a higher yield and lower lignin content, compared to the pulp obtained with sodium tungstate. However, the pulp obtained with sodium molybdate has lower brightness maybe because of the formation of colored

peroxygen complexes of molybdenum – Na_2MoO_6 (yellow permolybdate) and Na_2MoO_8 (red permolybdate).[38]

Physical properties of peracetic rape pulp

The peracetic rape pulps obtained during the delignification of rape straw with 10 wt% peracetic acid during 120 min, without and with the catalysts, were selected for further investigation of physical properties. The strength properties of handmade sheets from the peracetic pulps are presented in Figure 2. The results reveal that the three pulps differed from each other in their physical strength. The results indicate that the physical properties of the pulp obtained from non-catalytic pulping are very close to those of other non-woods: the breaking length, burst index and tear index for bagasse pulp are 4.7 km, 2.9 kPa·m^2/g and 7.6 mN·m^2/g, respectively, while the values of the same indexes for peracetic sunflower stalk pulp are 5.1 km, 2.4 kPa·m^2/g and 3.0 mN·m^2/g.[39,40] The handmade sheets produced with the peracetic pulp obtained with sodium molybdate achieved the best results for the breaking length, burst index and tear index due to better delignification. The improvement of the physical properties can be often explained by an increase in the number of hydroxyl bonds, which is achieved due to higher hemicellulose content. It is obvious that the use of catalysts makes it possible to reduce the hydrolytic transformations of polysaccharides, resulting in an increase of the strength characteristics of the fiber.

Physical properties of paper

To evaluate the feasibility of using rape stalks in the papermaking industry, paper sheets were made from peracetic rape pulp with different percentage of kraft pulp in combination with cationic starch and kaolin. The results obtained for the properties of the handmade sheets of writing paper are shown in Table 2.

It was found out that the paper made from peracetic pulp has a smoother and more elastic surface in comparison with kraft pulp. According to the results, the use of 100% kraft pulp in the composition of writing paper gives the best values of strength properties.

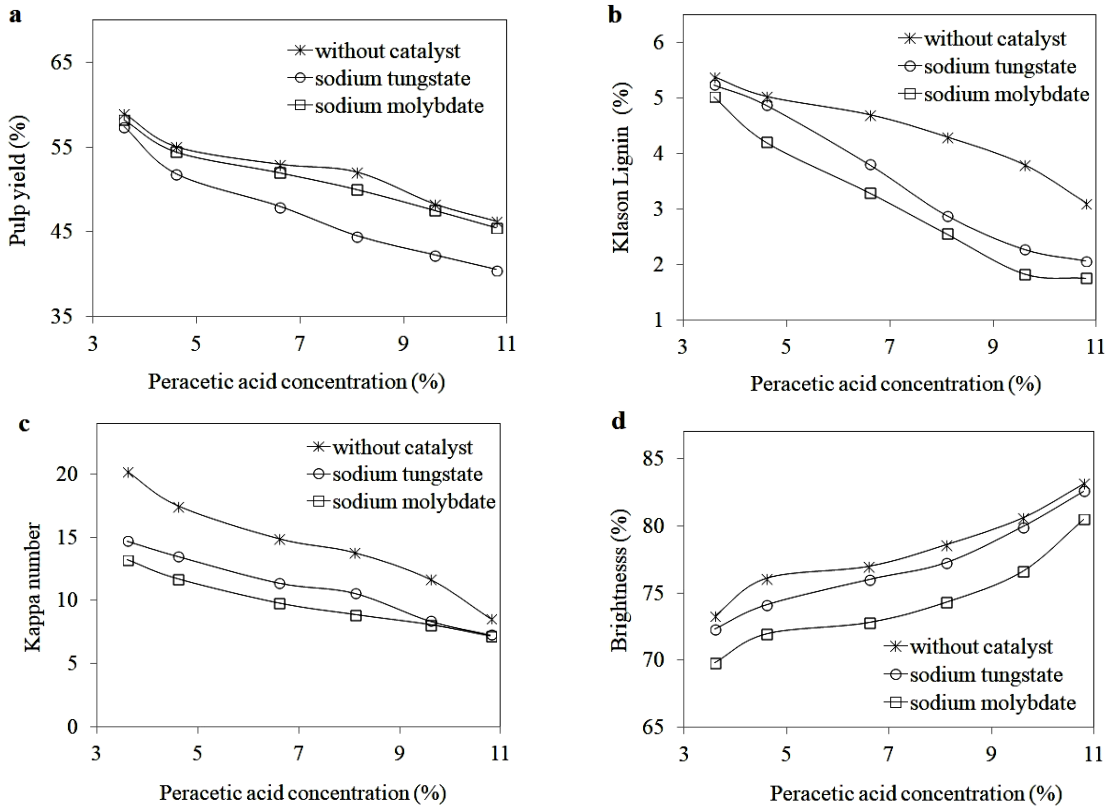

Figure 1: Effect of peracetic acid concentration on the properties of peracetic rape pulp: pulp yield (a), Klason lignin (b), Kappa number (c) and brightness (d)

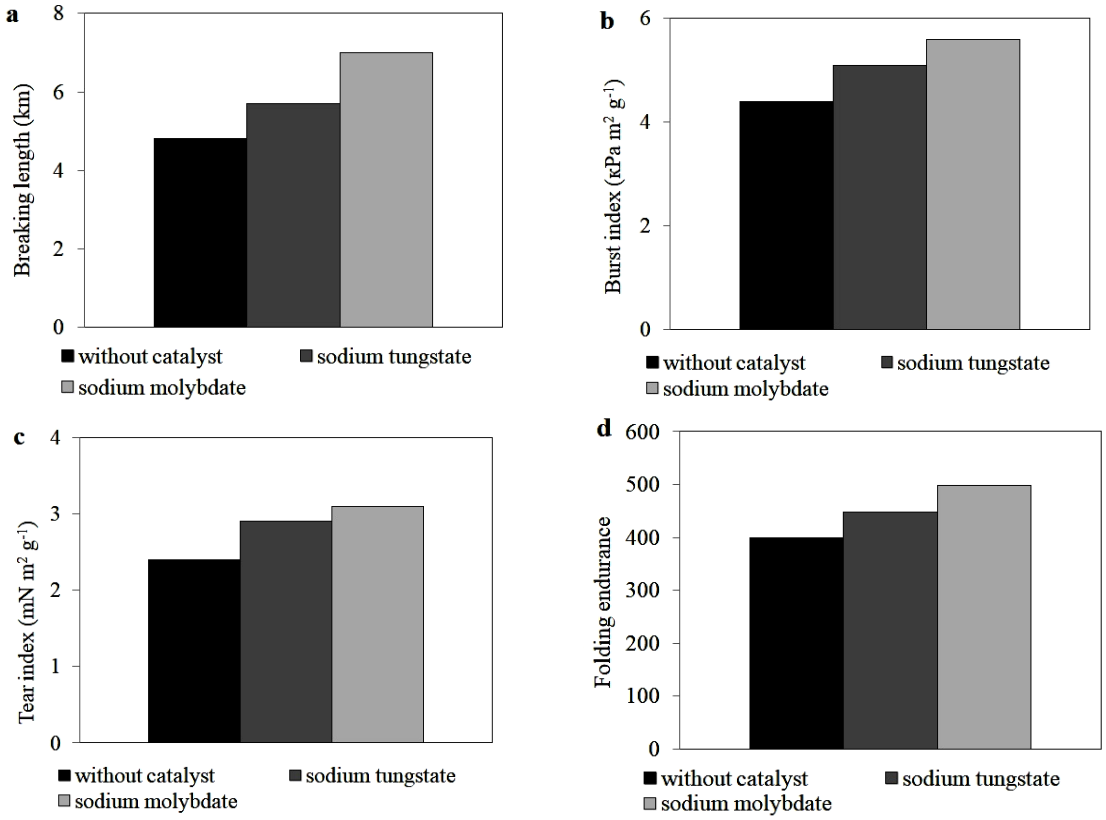

Figure 2: Physical properties of peracetic pulps: breaking length (a), burst index (b), tear index (c) and folding endurance (d)

A decrease in breaking length, folding endurance, tear index, for constant grammage and thickness, was noted with growing content of rape pulps, because of the length of the fibre (Table 3). As can be seen from the data Table 2, the maximum values for strength properties were obtained for the paper made from rape pulp with the addition of sodium molybdate.

Using the mentioned pulp in the amount of 25% does not lead to a significant decrease in physical properties.

Table 2
Physical properties of paper sheets

Pulping catalyst	Paper composition PRP/kraft pulp (%)	TH (mm)	D (g cm^{-3})	BL (km)	FE (df)	TI (mN m^2 g^{-1})	Br (%)
Without catalyst	100/0	0.091	0.82	2.2	28	0.65	76.7
	75/25	0.093	0.80	2.5	32	0.76	77.1
	50/50	0.093	0.80	2.7	36	0.80	78.3
	25/75	0.094	0.79	3.3	41	0.92	78.7
Na_2WO_4	100/0	0.091	0.82	3.5	39	0.60	74.0
	75/25	0.091	0.82	3.6	41	0.72	74.4
	50/50	0.094	0.79	3.7	45	0.76	75.9
	25/75	0.094	0.79	3.8	48	0.88	78.5
Na_2MoO_4	100/0	0.091	0.82	3.9	47	0.96	70.2
	75/25	0.093	0.80	4.1	49	0.96	71.6
	50/50	0.091	0.82	4.2	51	1.00	73.0
	25/75	0.093	0.80	4.3	53	1.04	73.6
-	0/100	0.093	0.80	4.3	51	1.12	82.2

PRP – peracetic rape pulp, TH – thickness, D – density, BL – breaking length, FE – folding endurance, TI – tear index, Br – brightness

Table 3
Fiber length distribution for different pulps (%)

Fiber length (mm)	Peracetic rape pulps			Bleached kraft pulp
	Without catalyst	Na_2WO_4	Na_2MoO_4	
0.02-0.19	1.05	0.41	0.23	0.09
0.20-0.40	22.83	34.09	20.87	5.22
0.41-0.60	38.17	26.31	37.05	17.69
0.61-1.19	28.90	20.75	31,43	22.55
1.20-2.00	7.85	17.54	9.80	22.03
2.01-3.00	1.20	0.91	0.62	20.51
3.00-7.00	0	0	0	11.91

The morphological properties of peracetic and kraft pulp fibers are shown in Table 3. The investigation of the fiber length shows that nearly 90% of the fibers from rape pulp obtained without catalyst have a length from 0.02 to 1.20 mm, nearly 8% of the fibers have a length from 1.20 to 2.00 mm, and only nearly 1% of the fibers have a length of more than 2 mm. The fiber length of the pulps obtained with sodium molybdate and sodium tungstate differs from that of peracetic pulp, and is characterized by the presence of greater percentages of the longest fibres. The results also indicate that the pulps from rape straw contained fibers with intermediate fibre length, lower than those of pine kraft pulp, but very close to those for hardwood (the fibre length for eucalyptus wood depends on the species and lies in the range from 0.76 to 1.01 mm).[41]
The results on physical properties suggest that rape straw could be considered as a promising resource for obtaining pulp, which can be used for production of paper and cardboard.

CONCLUSION

This work describes the procedure for obtaining pulp from rapeseed straw using peracetic treatments. The delignification of the initial raw material, using a catalyst, allowed preparing pulp with low lignin content and high brightness. A comparison of the impact of various catalysts indicated that sodium molybdate exhibits better activity in the delignification process of rape straw with a peracetic acid solution. It was found out that increasing the concentration of peracetic acid, in all the cases, reduced the content of lignin and increased the brightness of the peracetic rape pulp. The physical properties of the pulp and paper investigated in this study were found to be close to those reported in the literature for other agricultural residues.

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