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MODELLING OF PULP PROPERTIES DURING DELIGNIFICATION ON NON-WOOD MATERIALS BY DMF

AHMAD GHOZATLOO and J. MOHAMMADI-ROVSHANDEH*

Faculty of the Research Institute of Petroleum Industry (RIPI)
PO Box 14665-1998, Iran
**Caspian Faculty of Engineering, University College of Engineering,*
University of Tehran, PO Box 43841-119, Rezvanshahr, Gilan, Iran

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As an environmentally friendly solvent, dimethylformamide (DMF) creates mild pulping conditions and high selectivity during non-wood materials pulping. When using an aprotic DMF solvent, the main delignification reaction is hydrolysis. Pulping of non-wood materials by DMF was studied for stating the effects of the main cooking variables – such as cooking temperature, cooking time and DMF ratio – on the pulp properties, during DMF pulping. The responses of pulp properties to the process variables were analyzed with a MINITAB statistical software. The results obtained showed that acceptable pulp properties of non-woods could be achieved at 210 °C, 150 min and 50% DMF ratio, and also that the cooking temperature had a significant effect on pulping of DMF. The main factors involved in the analysis revealed that an optimum pulp from non-wood materials should have the following characteristics: 54.8% (yield), 82% (holocellulose), 66.3% (cellulose), 84.7% (α-cellulose), 41.4 (kappa number) and 1241 cm^3/g (viscosity).

Comparatively with the pulp properties of Kraft and DMF, it can be asserted that, basically, DMF plays a positive role, reducing cellulose degradation in the obtained pulp. Consequently, the protective action of DMF on non-wood materials against degradation under Kraft pulping conditions is considered as the main reason of the fairly high yield of DMF pulping and of the superior properties, compared to those of Kraft.

Keywords: DMF, organosolv pulp, non-wood materials, viscosity, multiple linear regressions, MINITAB

INTRODUCTION

In conventional pulping processes (Kraft, soda and alkaline sulphite), the lignin structure is broken into smaller parts before it dissolves in the cooking liquor while, in DMF without chemical reactions, lignin will not be dissolved.[1] In the same way, process variables – such as cooking time and cooking temperature – also affect the reactions.[2] Compared with the conventional pulping processes, organosolv pulping delignifies non-wood materials more easily than softwoods and hardwoods,[3] because the lignin of non-wood materials is more reactive, being present in smaller amounts than the lignin of softwoods and hardwoods.[1] The process by which raw materials are pulped produces large amounts of highly polluting wastewater, especially sulphite- and sulphate-based processes,[4] which called for environment-friendly processes, such as the organosolv ones, known as reducing the unpleasant effects.[1]

In spite of the numerous investigations on non-wood materials by different pulping processes, little research has been conducted on the pulping of non-wood materials with DMF as an organic solvent. Organosolv pulping is a chemical pulping method in which delignification of non-wood materials, such as bagasse and straws, is done by an organic solvent plus a water system.[5] One of the main drawbacks of low molecular organic solvents is the high pressure generated during pulping. Besides, they are highly volatile and inflammable. Also, the investments required to reduce the risk associated with the use of alcohol would increase the production costs.[5] A solvent with medium boiling points can be used for pulping non-wood resources.[6]

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As an organic solvent, DMF has a medium boiling point (152-154 °C), which causes a medium condition in the pulping of non-wood materials – as actually confirmed by some preliminary experiments. This explains the utilization of DMF for pulping non-wood materials.[3]

Generally, organosolv pulping has low effects on carbohydrate degradation, DMF showing good selectivity in the delignification reaction. By protic solvents, such as alcohols, in the absence of acids and bases, the main reactions occurring during pulping are hydrolysis and, to a lower extent, solvolysis.[1] The quality of organosolv pulps is not competitive with that of Kraft pulps. Particularly in alcohol pulping, pulp quality can be improved by adding alkali to the system. Pulping with the new solvent – DMF – shows numerous advantages, such as obtaining a pulp that contains more hemicelluloses, a lower cellulose degradation, a high yield, low kappa number, high brightness and good strength.[5]

A central composition design (CCD) was applied in the present investigation to study the influence of cooking variables on various properties (cooking time, cooking temperature and DMF ratio) of the non-wood materials with DMF-water mixtures.[7] So far, few authors have used a factorial design to develop empirical models involving several independent variables, to identify the variation patterns in the dependent variables of various pulping processes. In this respect, organosolv pulping has been extensively studied.[7] Wheat straw, bagasse and rice straw are important non-wood materials considered in this context.[1,3,5]

EXPERIMENTAL

Methods of pulp analysis

The analysis of pulp variables (alpha cellulose and kappa number) was performed according to Tappi Standard Methods,[8] namely: holocellulose – as determined by Wise's sodium chlorite method,[9] cellulose – according to Kurscher and Hoffner's nitric acid method[10] and pulp viscosity was measured in a cupri-ethylenediamine (CED) solution, according to a SCAN-CM 15:88 standard.[11] Pulp yield was determined[3] gravimetrically, following a drying stage at 100 ±1 °C, after 24 h.

Pulping procedure

In the experiments, DMF was used as an organic solvent for reed delignification. In each experiment, 200 g of dried reed were charged into the digester and the mixture of DMF with water as cooking liquor was set to 30/70, 50/50 and 70/30%, at a solid/liquor ratio of 1/10% by weight. The cooked pulp was washed with warm pure water and prepared for the experiments. The cooking temperature and cooking time used in the different experiments were 190, 200 and 210 °C and 120, 150 and 180 min, respectively.

Experimental design for pulping conditions

Optimization is an essential problem in the investigation and development of competitive industrial processes.[12] The pulping processes have been modelled in many ways, to derive equations estimating the quality of the pulping results as a function of the process variables, and to optimize the operating conditions.[1] According to other studies on non-wood pulping, a central composite design was used to determine the number of experiments and conditions.[1,3,5] Therefore, the total number of experiments (N) required for the 3 independent variables (k = 3): cooking temperature (T); cooking time (t) and DMF ratio (D) was 15, according to the following equation:[13]

$$N = 2^k + 2k + 1 \qquad (1)$$

where k is the number of independent variables. To facilitate a direct comparison of the coefficients and to visualize the effects of the individual independent variables on the response variable, the values of the independent variables should be normalized,[3] according to the following equation:

$$X_n = 2(X - X_{mean})/(X_{\max} - X_{\min}) \qquad (2)$$

where X_n is the normalized value of T, t or D; X is the absolute experimental value of the variable concerned, X_{mean} is the mean of all experimental values for the variable in the equation, $X_{\max}$ and $X_{\min}$ are the maximum and minimum value of the variable, respectively. Equation (2) normalizes all values of the independent variables at 3 levels: (-1), (0) and (+1). The experimental data were fitted to the following second-order polynomial:[14]

$$Z = a + bX_T + cX_t + dX_D + eX_T^2 + fX_t^2 + gX_D^2 + hX_T X_t + iX_T X_D + jX_t X_D \qquad (3)$$

where Z is the response variable to each pulp property, X_T, X_t and X_D are the normalized values of T, t and D, respectively, while letters a to j denote constants. The results of these 15 experiments and the corresponding normalized values for the independent variables of reed pulp are given in Table 1.

DMF pulping of some important non-wood materials, such as bagasse, rice straw and wheat straw has been studied[1,3,5] by several authors (Table 2). In this work, the same method was applied to evaluate reed pulp properties. For example, CCD was used to determine the number of experiments, and the MINITAB software – for modelling the reed pulp properties.

Table 1
Values of independent variables and chemical properties of reed pulp obtained in pulping with the proposed experimental design

X_T	X_t	X_D	Y (%)	H (%)	C (%)	αC (%)	KN	V (cm^3/g)
1	1	1	57.2	78.4	61.3	77.9	44.2	1188
-1	1	1	65.4	76.4	62.3	71.1	58.6	1205
1	-1	1	58.3	79.9	60.5	74.8	47.6	1198
-1	-1	1	69.8	79.6	61.7	70.3	58.9	1190
0	0	1	63.4	80.3	59.6	71.6	52.7	1212
1	1	-1	53.7	81.5	66.3	78.8	49.1	1204
-1	1	-1	58.6	77.1	64.5	69.7	53.6	1233
1	-1	-1	56.1	80.2	61.9	77.9	56.1	1219
-1	-1	-1	63.7	83.2	61.9	70.6	60.3	1188
0	0	-1	58.1	78.6	59.4	75.4	51.7	1213
-1	0	0	63.7	77.5	65.2	73.6	55.4	1198
0	-1	0	59.4	79.1	63.8	75.9	57.2	1254
1	0	0	55.3	80.3	62.5	78.8	42.1	1196
0	1	0	59.8	82.6	64.2	77.9	45.6	1255
0	0	0	60.4	76.3	61.3	78.1	49.6	1199

X_T – normalized cooking temperature; X_t – normalized cooking time; X_D – normalized DMF ratio; Y – yield; H – holocellulose; C – cellulose; αC – alpha cellulose; KN – kappa number; V – viscosity

Developing models

Based on the data of Table 2, some main models for modeling the DMF behavior of non-wood materials during pulping were obtained. For using an average value for each response of the pulp properties of some important non-wood materials, a main model for predicting each value of the pulp properties of non-wood materials during DMF pulping should be first obtained.

The geometrical mean for the value of responses (expressed percentually), such as yield, holocellulose, cellulose and alpha cellulose, along with the mathematical mean for the values of pulp properties expressed numerically, such as kappa number and viscosity, should be employed. For calculating the geometric mean value, the following equation was used:[15]

$$GA = (\prod_{i=1}^{n} x_i)^{\frac{1}{n}} \tag{4}$$

where GA is the geometrical mean, x_i is the absolute value of each response and n is the number of responses. According to Table 2, three value responses are obtained for each pulp property, one for bagasses, another for rice straw and the other for wheat straw. Therefore, Equation (4) is reduced to:

$$GA = (x_1 * x_2 * x_3)^{\frac{1}{3}} \tag{5}$$

The values of the geometrical means of yield, holocellulose, cellulose and alpha cellulose are shown in Table 3. In addition, the mathematical mean is calculated with Equation (6):

$$MA = (\sum_{i=1}^{n} x_i) / n \tag{6}$$

where MA is the mathematical mean, x_i is the absolute value of each response and n is the number of responses. In calculating the mathematical mean similarly with the calculation of the geometrical mean, three value responses for each property of pulp (kappa number and viscosity) are obtained. Therefore, Equation (6) is reduced to the following equation:

$$MA = \frac{(x_1 + x_2 + x_3)}{3} \tag{7}$$

The mathematical mean values of kappa number and viscosity are also included in Table 3; consequently, the mean pulp properties for bagasse, rice straw and wheat straw obtained by DMF pulping are shown in Table 3.

The obtained value of responses allows developing mathematical estimation models for each response, which are subsequently used to characterize the nature of the response surface.[3] The MINITAB software was used[16] to conduct a multiple linear regression analysis involving all terms of Eq. (3). The stepwise forward selected method also includes statistics that can be used for the model developed.[1]

Table 2
Values of independent variables and chemical properties of
bagasse (B), rice straw (R) and wheat straw (W) by DMF pulping

Normalized variables			Y (%)			H (%)			C (%)			αC (%)			KN			V (cm^3/g)		
X_T	X_t	X_D	*B*	*R*	*W*	*B*	*R*	*W*	*B*	*R*	*W*	*B*	*R*	*W*	*B*	*R*	*W*	*B*	*R*	*W*
1	1	1	58.2	58.2	52.6	94.0	73.3	73.9	63.5	62.7	65.0	70.6	86.6	75.1	27.5	44.5	47	1125	1201	1255
-1	1	1	73.7	63.7	64.5	88.4	67.1	72.7	68.3	67.3	69.0	58.4	84.7	73.0	64.8	57	52	1129	1254	1341
1	-1	1	59.5	58.1	53.0	96.3	75.4	80.4	68.2	67.5	69.3	73.2	87.3	75.3	34.8	51	63	1127	1296	1330
-1	-1	1	82.5	67.6	66.6	76.9	66.9	68.9	63.1	64.1	65.7	51.5	82.8	71.8	80.3	70	61	1146	1304	1335
0	0	1	60.1	60.3	60.0	60.1	75.3	76.5	61.9	60.1	62.6	69.9	85.9	73.9	56.2	50	52	1204	1254	1294
1	1	-1	51.7	51.5	50.3	91.1	72.9	74.4	65.2	64.1	65.7	74.8	91.6	82.6	35.2	45	50	1101	1236	1248
-1	1	-1	63.5	56.5	57.4	89.0	70.2	71.6	61.5	62.1	64.6	67.9	88.2	76.2	59.5	50	54	1215	1278	1304
1	-1	-1	61.4	53.9	51.1	94.6	70.2	74.0	66.1	65.6	67.2	74.1	90.1	79.0	62.0	48	52	1165	1254	1269
-1	-1	-1	77.5	59.6	57.9	78.5	69.6	75.8	68.3	67.5	69.2	63.9	85.2	73.2	82.8	50	58	1219	1200	1290
0	0	-1	59.6	56.8	54.5	94.2	74.2	72.8	60.7	60.3	62.9	72.9	87.5	75.5	57.0	48	57	1132	1345	1281
-1	0	0	80.4	60.3	60.9	84.2	75.3	77.3	65.3	62.1	64.7	73.0	84.8	73.0	56.5	55	59	1212	1266	1343
0	-1	0	63.3	58.9	55.9	90.7	72.1	77.0	67.4	66.3	68.0	72.6	88.2	76.2	55.5	55.1	57	1265	1304	1334
1	0	0	55.7	54.1	53.1	94.2	71.3	77.2	68.8	67.6	69.3	79.8	92.1	84.1	31.2	41	52	1194	1312	1264
0	1	0	57.3	57	55.2	91.3	73.4	77.5	67.4	66.3	68.0	72.3	90.3	79.3	40.5	47	60	1145	1247	1269
0	0	0	60.1	57.7	57.0	93.3	75.9	85.3	68.2	69.3	71.0	76.6	89	77.0	47.4	41.5	49	1166	1250	1285

X_T – normalized cooking temperature; X_t – normalized cooking time; X_D – normalized DMF ratio;
Y – yield; H – holocellulose; C – cellulose; αC – alpha cellulose; KN – kappa number and V – viscosity;
B – bagasse; *R* – rice straw; *W* – wheat straw

Table 3
Mean values of pulp variables by DMF pulping for non-wood materials

X_T	X_t	X_D	$\overline{Y}$ (%)	$\overline{H}$ (%)	$\overline{C}$ (%)	$\overline{\alpha C}$ (%)	$\overline{KN}$	$\overline{V}$ (cm^3/g)
1	1	1	56.3	79.9	63.7	77.1	39.7	1194
-1	1	1	67.1	75.5	68.2	71.2	57.9	1241
1	-1	1	56.8	83.6	68.3	78.4	49.6	1251
-1	-1	1	71.9	70.8	64.3	67.4	70.4	1262
0	0	1	60.1	70.2	61.5	76.3	52.7	1251
1	1	-1	51.2	79.1	65.0	82.7	43.4	1195
-1	1	-1	59.0	76.5	62.7	77.0	54.5	1266
1	-1	-1	55.3	78.9	66.3	80.8	54.0	1229
-1	-1	-1	64.4	74.5	68.3	73.6	63.6	1236
0	0	-1	56.9	79.8	61.3	78.4	54.0	1253
-1	0	0	66.6	78.8	64.0	76.7	56.8	1274
0	-1	0	59.3	79.5	67.2	78.7	55.9	1301
1	0	0	54.3	80.3	68.6	85.2	41.4	1257
0	1	0	56.5	80.4	67.2	80.3	49.2	1220
0	0	0	58.2	84.6	69.5	80.7	46.0	1234

$\overline{Y}$ – geometrical mean of yields; $\overline{H}$ – geometrical mean of holocelluloses; $\overline{C}$ – geometrical mean of celluloses; $\overline{\alpha C}$ – geometrical mean of alpha celluloses; $\overline{KN}$ – mathematical mean of kappa numbers; and $\overline{V}$ – mathematical mean of viscosities

The obtained value of responses allows developing mathematical estimation models for each response, which are subsequently used to characterize the nature of the response surface.[3] The MINITAB software was used[16] to conduct a multiple linear regression analysis involving all terms of Eq. (3). The stepwise forward selected method also includes statistics that can be used for the model developed.[1]

Eqs. (8) to (13) are reduced models for each response:

Yield
$$\overline{YI} = 58.2 - 5.51X_T + 2.54X_D - 1.76X_t + 2.1X_T^2 - 1.13X_TX_D + 0.7X_TX_t \tag{8}$$

Holocellulose
$$\overline{H} = 79.78 + 2.23X_T - 0.09X_T^2 - 3.2X_D^2 - 1.22X_D \tag{9}$$

Cellulose
$$\overline{C} = 66.31 - 3.3X_D^2 + 2.5X_t^2 - 0.1X_TX_t \tag{10}$$

Alpha cellulose
$$\overline{\alpha C} = 80.86 + 3.83X_T - 2.21X_D + 0.94X_t - 3.5X_D^2 - 1.34X_t^2 + 0.83X_TX_t \tag{11}$$

Kappa number
$$\overline{KN} = 48.91 - 7.51X_T - 4.88X_t + 2.4X_t^2 + 3.2X_D^2 - 2.29X_TX_D \tag{12}$$

Viscosity
$$\overline{V} = 1257 - 15.3X_T - 16.3X_t - 19X_D^2 - 12.5X_TX_t \tag{13}$$

Also, the coefficient estimates for each term of the developed models have been shown for every dependent variable. The steepest ascent method was applied to Eqs. (8) to (13), for determining the highest properties over the ranges of the studied process variables (normalized values from -1 to +1 for all).[17] These models allow the estimation of the variation of non-wood pulp properties with changes in each independent variable, which is consistent with the other two variables over the considered range. The accuracy of each model developed on the basis of such data is shown with some regression values, such as *S*, *R-sq*, *R-sq (adj)* and *Mallow C-p*. For each developed model, these regression values show the rate of accuracy in predicting pulp properties. The values of regression analysis for the developed models, such as *S*, *R-sq*, *R-sq (adj)*, and *Mallow C-p*, were summarized in Table 4.

Generally, the smaller the *S* and the larger the *R* and *R (adj)*, the better the model fits the data.[1] *Mallow C-p* should be close to the number of predictors contained in the model. According to Table 4, the results obtained confirm the adequacy of the fitted models, where all models – with the exception of *R-sq* – are at a level of 90 or more.

After developing the models, the advance rate of model prediction should be determined to estimate the accuracy of the value of pulp properties. Therefore, the deviation rate of the model response and the experimental data of non-wood materials were calculated by measuring the error between these values. For calculating each error between the model response and the experimental data for reed pulp, the following equation was used:[15]

$$error = \frac{E-M}{E} * 100 \qquad (14)$$

Where E is the absolute value of the experimental data and M is the response of the model to the same condition. For example, at $X_T = 1$, $X_t = 1$, and $X_D = 1$, the value of yield based on Eq. (8) is of 55.7, while the value of yield of reed pulp based on Table 1 is of 57.2, so that the error between these values is calculated with Eq. (14):

$$error_Y = (57.2 - 55.7)/57.2 * 100 = 2.7\%$$

(marked in Table 5 with *).

For this reason, Table 5 shows the errors between the developed model responses and the experimental data of the reed pulp from Table 1.

Table 4
Values of regression analysis for the developed models

	$\overline{Y}$	$\overline{H}$	$\overline{C}$	$\overline{\alpha C}$	$\overline{KN}$	$\overline{V}$
S	1.46	2.17	2.37	1.75	1.71	1.21
R-sq	95.09	92.12	90.72	91.32	94.21	96.11
R-sq (adj)	90.13	89.39	87.13	88.64	89.66	90.47
Mallow C-p	5.2	3.1	2.6	4.9	4.7	3.4

S – estimate of standard deviation of the error term in the model; *R-sq* – ratio of variation in response data explained by the model; *R-sq (adj)* – modified *R*, adjusted for the number of predictors in the model; *Mallow C-p* – another statistics for assessing how well the model fits the data

Table 5
Errors between developed model responses and experimental data on reed pulp

X_T	X_t	X_D	$error_Y$ (%)	$error_H$ (%)	$error_C$ (%)	$error_{\alpha C}$ (%)	$error_{KN}$ (%)	$error_V$ (%)
1	1	1	2.7*	-8.6	-6.7	-1.9	9.9	-0.5
-1	1	1	-3.3	-6.2	-5.3	4.1	-1.4	-3.7
1	-1	1	2.7	-6.6	-8.4	-3.9	-4.2	-4.5
-1	-1	1	-2.3	-1.9	-6.0	0.6	-17.5	-5.6
0	0	1	4.2	-3.6	-5.7	-5.0	1.1	-2.1
1	1	-1	3.5	-4.2	1.3	-6.4	9.6	0.8
-1	1	-1	-1.0	-5.5	-1.7	-4.2	-2.3	-1.3
1	-1	-1	2.0	-5.9	-6.0	-5.5	3.4	-2.7
-1	-1	-1	-2.2	2.2	-5.7	-5.2	-7.1	-5.8
0	0	-1	4.2	-5.9	-6.1	-5.5	-0.8	-2.1
-1	0	0	-3.3	-4.7	-1.7	-3.4	-1.8	-6.2
0	-1	0	-0.9	-5.1	-7.9	-4.8	1.8	-1.5
1	0	0	0.9	-5.8	-6.1	-8.7	1.7	-3.8
0	1	0	5.6	-0.6	-7.2	-2.1	-1.8	1.1
0	0	0	3.6	-8.9	-8.2	-3.5	1.4	-4.8

$error_i$ – error between the developed model and the value of reed pulp;
*the method of calculation in this case has been described in the experimental section

Table 6
Total error between model response and absolute value of pulp properties

Model	$\overline{Y}$	$\overline{H}$	$\overline{C}$	$\overline{\alpha C}$	$\overline{KN}$	$\overline{V}$
Total error (%)	2.5	4.3	-3.8	2.9	2.9	-2.5
Equation No.	(8)	(9)	(10)	(11)	(12)	(13)

$\overline{Y}$ – yield; $\overline{H}$ – holocellulose; $\overline{C}$ – cellulose; $\overline{\alpha C}$ – alpha cellulose; $\overline{KN}$ – kappa number and $\overline{V}$ – viscosity

According to Table 5, 15 errors occur for each model, so that, for estimating the total error for each model, a total average error should be calculated. Since the type of errors is expressed in percent form, the geometrical mean should be used. Therefore, the following equation was used:[15]

$$total\ \ error = (\prod_{i=1}^{n} e_i)^{\frac{1}{n}} \qquad (15)$$

where e_i is the absolute value of error for each model and n is the number of errors ($n = 15$).

Consequently, Table 6 shows the total error between models response and the absolute value of each pulp property on the basis of Eq. (15).

According to the absolute value of the total errors calculated between the models and the experimental data for reed pulp, it can be seen that the precision of models for predicting the pulp properties of non-woods was done with a maximum error of 4.3%, which means that the developed models [Eqs. (8) to (13)] grant good prediction for the properties of non-woods subjected to DMF pulping.

RESULTS AND DISCUSSION

Considering the importance of the cellulose structure in pulp for predicting other pulp properties and also for showing the effects of DMF behavior during pulping, this section focused on the cellulose amount and on its structure in the obtained pulp of non-wood materials, on the basis of statistical analysis and of the developed models.

Pulp cellulose is organized into fibrils, surrounded by a matrix of lignin and hemicelluloses.[18] The material is a linear polymer of anhydroglucose units divided into alpha, beta and gamma cellulose, on the basis of its polymerization degree. Generally, alpha cellulose indicates a non-degraded, higher molecular weight cellulose content in pulp, while beta cellulose indicates the rate of degraded cellulose, and gamma cellulose indicates the approximate hemicellulose contents in the pulp.[19] The investigation of these components permitted to determine and compare the amount of cellulose degradation. Under acidic and alkaline pulping conditions (Kraft, soda and alkaline sulphite), the degradation of the cellulose structure occurs. Acidic hydrolysis of the glycosidic bonds of cellulose is also important. The predominant degradation reaction performed under alkaline conditions is the peeling reaction, through which some glucose units are removed from the cellulose molecule.[3] By such reactions, the carbohydrate-lignin etheric linkage is broken, while the α-O-4 and β-O-4 bonds of the lignin molecules subjected to some hydrolysis and some small lignin fragments are formed. These fragments can be dissolved in the solvent system. Thus, as an aprotic solvent, DMF has no direct effect on the delignification reaction, having, nevertheless, a protecting effect on cellulose degradation through hydrolysis.[1]

Cellulose content and structure

It seems that, as an organic solvent, DMF has a major effect on the cellulose percentage in the obtained pulp, related to an increased DMF ratio, which reduced both the hydrolytic reactions and cellulose chain degradation. However, increasing of the cellulose contents alone does not improve the properties of the obtained pulp. Consequently, the study of alpha cellulose is more important, showing the DMF behavior during pulping.

α-cellulose, representing the main part of cellulose, has chains built up of more than 150 units.[20] It is considered as an important factor for investigating the quality of the obtained pulp. Statistical analysis of non-wood pulps shows that, out of the three factors affecting α-cellulose, the most effective one is cooking temperature – almost 8.12% (7.14 on wheat straw, 11.56 on bagasse and 4.8%, respectively, on rice straw).[1,3,5] Similarly with statistical analysis, the effect of cooking time on the α-cellulose percentage is higher than that of the DMF ratio.

The interaction of cooking time and cooking temperature on the long chain of cellulose (α-cellulose) in the pulp is shown in Figure 1. As obvious, increasing both cooking time and cooking temperature has positive effects on the α-cellulose percentage, at a high constant level of the DMF ratio. On the other hand, pulping under conditions of high temperature and long cooking time can be used for removing most lignin from pulp, without any degradation of the main chain of cellulose, in the pulp obtained from non-wood materials in the presence of DMF.

The holocellulose amount shows the content of hemicellulose and cellulose in pulp[3] (Table 3). The retention of holocellulose, particularly polysaccharides (hemicelluloses), during delignification or bleaching of pulp has a critical influence on the yield and properties of pulp.[21] Statistical analysis showed the positive effect (2.23) of cooking temperature on holocellulose, according to Eq. (9).

The responses of holocellulose to cooking time and temperature, at a DMF ratio of 70%, are illustrated in Figure 2, according to which, at high, constant DMF ratio, the holocellulose content in pulp tends to increase with increasing cooking temperature on all cooking time levels. More precisely, increasing of cooking temperature did not degrade the cellulose structure in the pulp of non-wood materials.

Generally, in pulping processes, viscosity is a function of cellulose fiber degradation.[11] The results of viscosity can be applied for estimating the extent of cellulose degradation during cooking.[11] The advantages of DMF, comparatively with conventional pulping, include higher retention of carbohydrates and low degradation of cellulose (assessed by the yield and viscosity values recorded in other processes).

When comparing the effect of DMF – by the Kraft process – on reducing cellulose degradation of non-wood pulps, a great difference is observed between the amounts of viscosities that can be attained.[1] Thus, basically, DMF reduces cellulose degradation, an aspect that should be intensely used to improve pulp production in related industries. The application of an increased DMF ratio had a very significant effect on reducing cellulose degradation, which means that pulp viscosity increased with increasing the DMF ratio under mild cooking conditions. The main effects of cooking temperature, DMF ratio and cooking time on viscosity are shown in Table 3 and Eq. (11). The error percentage of the experimental viscosity values, with respect to the values of the equation, was negligible (Table 4), meaning that the highest error in the percentage of viscosity was of only 1.8% – according to Eq. (11) Apparently, cooking temperature was the most influential factor in relation to the viscosity of non-wood pulps, followed by cooking time.

As shown in Figure 3, pulp viscosity decreases with increasing cooking temperature on all DMF ratio levels and high, constant cooking time. On the other hand, cooking temperature was the most influential factor in decreasing the pulp viscosity of non-wood pulps. It is interesting to observe that, comparatively with the other two main factors, cooking temperature was the main driving force in damaging the cellulose structure of non-wood pulps, based on decreasing related viscosity.

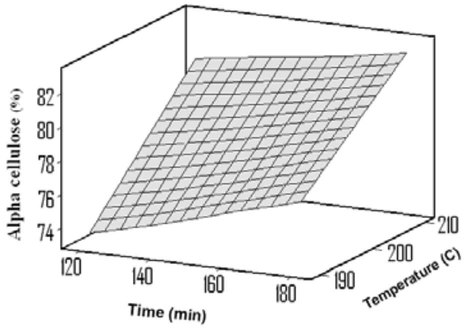

Figure 1: α-cellulose variation with cooking time and temperature at high constant DMF ratio

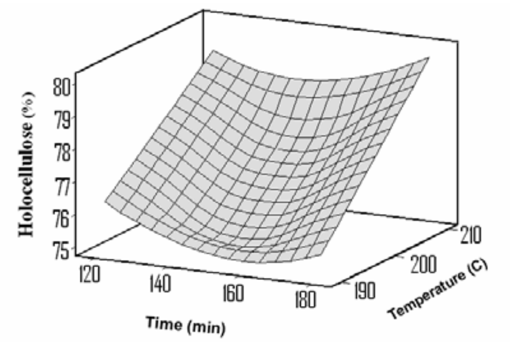

Figure 2: Holocellulose variation with cooking time and temperature at high, constant DMF ratio

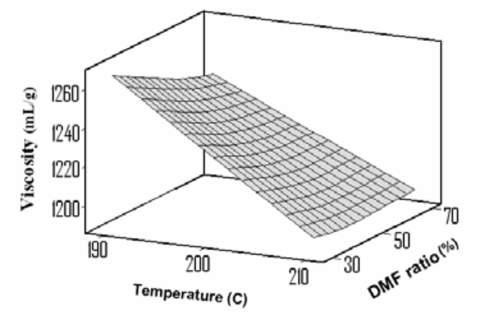

Figure 3: Pulp viscosity variation with cooking temperature and DMF ratio at high, constant time

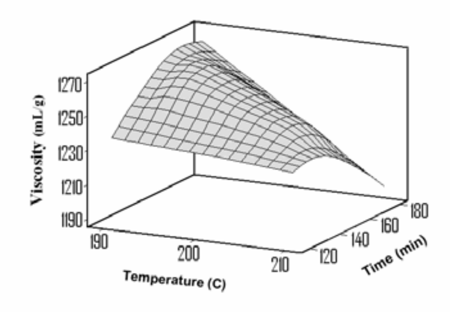

Figure 4: Pulp viscosity variation with cooking temperature and time at low, constant DMF ratio

For a short cooking time, an increase in cooking temperature caused a decrease in pulp viscosity, all DMF rates having no considerable effect on decreasing pulp viscosity. According to Figure 4, when the DMF ratio was low (30%), pulp viscosity decreased with increasing cooking time and cooking temperature – therefore, under high pulping conditions (210 ºC and 180 min), the maximum degradation of cellulose occurred.

CONCLUSIONS

Interesting results have been attained by using new solvents, such as DMF, in pulping, *e.g.* pulp presenting more hemicellulose, lower cellulose degradation, high yield, low residual lignin content, high brightness and good strength was obtained.[7,22]

The advantages of non-wood pulping by DMF include medium pressure in the digester, a higher retention of carbohydrates, and low degradation of the cellulose chain in pulp.[31] Consequently, DMF has a significant effect on reducing carbohydrate degradation during cooking. For all values of cooking temperature and time, the increase of the DMF ratio improved the yield of non-wood pulp. Thus, it may be observed that cellulose degradation was reduced during organosolv delignification of non-wood fibers by hydrolysis reactions, under the aprotic conditions of DMF as a solvent. Generally, DMF pulping has a low effect on carbohydrate degradation and a good selectivity in the delignification reaction; when using an aprotic DMF solvent, the only delignification reaction is hydrolysis.

According to all experimental data and statistical results, optimum conditions for DMF pulping are obtained at 200 °C, 150 min and 50% DMF ratio, for producing a pulp from easy-to-bleach non-wood fibres with acceptable properties – the yield after bleaching being sometimes higher than that of Kraft pulp.

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