Study on Cellulose Degradation during Organosolv Delignification of Wheat Straw and Evaluation of Pulp Properties

Yaser Ziaie-Shirkolaee[1], Jamshid Mohammadi-Rovshandeh[1*]
Pejman Rezayati Charani[2], and Mohammad Bagher Khajeheian[1]

(1) Chemical Engineering Department, Faculty of Engineering, University of Tehran,
P.O. Box: 43841/119, Rezvanshahr, Guilan, Iran
(2) Iran Wood and Paper Co. (Chouka), P.O. Box: 43841/119, Rezvanshahr, Guilan, Iran

A B S T R A C T

Pulping of wheat straw by dimethylformamide was studied in order to investigate the effects of the cooking variables temperature (190, 200, and 210°C), time (120, 150, and 180 min), and organic solvent ratio (30, 50, and 70%) of dimethylformamide (DMF+water) value on the degradation of cellulose and delignification of organosolv pulp. The SCAN viscosity was applied to estimate the extent of cellulose degradation produced by cooking condition and it was compared with Kraft pulp at equal content of residual lignin. Response of pulp properties to the process variables were analyzed using statistical software MINITAB 14. The process variables (cooking temperature and time) were set at low variables at high DMF ratio in order to ensure of the low cellulose degradation. Generally, the cooking temperature had a significant effect while the cooking time and DMF ratio had negligible roles. By the comparison of Kraft and organosolv pulps (higher SCAN viscosity of organosolv pulp than Kraft process under equal residual lignin and scanning electron microscopy images) it can be asserted that DMF basically has an improvement role on reducing the cellulose degradation of obtained from pulp. Consequently, the protective action of organosolv on non-cellulosic polysaccharides of wheat straw against degradation under Kraft pulping conditions is considered as the main reason of the fairly high yield of organosolv pulping.

(∗) To whom correspondence to be addressed:
E-mail: roshandeh@ut.ac.ir

INTRODUCTION

Organosolv (solvent-based) pulping is a chemical pulping method in which delignification of biomass (usually wood) is done by an organic solvent or solvent plus water system. In conventional cooking and organosolv cooking, the lignin structure is broken into smaller parts before it dissolves in the cooking liquor. No solvent or combination of solvents has yet been found that would dissolve lignin directly from the wood matrix. Without chemical reactions, lignin will not dissolve. One reason is that lignin forms chemical bonds with wood polysaccharides. Process variables such as cooking time and temperature also affect the reactions in the same way as in conventional cook-

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ing. The cleavage of ether bonds in the lignin structure is a key to delignification reaction [1].

The reactions taking place during alkaline organosolv cooking are similar to those in the corresponding conventional processes (Kraft, soda, and alkaline sulphite). At alkaline pH, alpha aryl ether bonds would be broken only in those phenyl propane units containing free phenolic hydroxyl groups.

Lignin undergoes condensation reactions under acidic and alkaline conditions. Condensation reactions such as the formation of carbon-carbon bonds and intermolecular condensation particularly hinder delignification and subsequent bleaching. As compared with conventional methods, organosolv cooking delignifies hardwoods and non-wood materials more easily than softwoods. This is because hardwood lignin is more reactive and is present in smaller amounts than softwood lignin.

Lignin and polysaccharides react differently in various delignification processes, affecting their selectivity. Hemicelluloses are attacked more easily than cellulose due to their amorphous state and lower degree of polymerization. For autohydrolysis, an important reaction is the cleavage of acetic acid from wood xylan at high temperature. This free acetic acid initiates the acid hydrolysis of lignin [2].

The process, by which raw materials are pulped, produces large amounts of highly polluting waste water, especially sulphite and sulphate based processes. These reasons have raised the need for new processes such as organosolv processes that reduce the unpleasant effects. Organosolv processes have been applied with varying success to hard and soft woods and also, to a lesser extent, to non-wood materials [3-7]. One of the main drawbacks of low molecular organic solvents is the high pressure generated during the pulping stage. Besides, they are highly volatile and flammable. The investments required to reduce the risk associated with the use of alcohol would increase the production cost [8,9]. Solvent with medium boiling points can be used for the pulping of lignocellulosic resources [10]. According to preliminary experiments and physico-chemical properties of dimethylformamide (DMF) as an organic solvent with a medium boiling point was used for the pulping of wheat straw. Wheat straw, bagasse, reed, and rice straw are the important non-wood fibres sources which have been studied in this context [2,10-13].

Cellulose of pulp is organized into fibrils, which are surrounded by a matrix of lignin and hemicelluloses [14]. This material is a linear polymer of anhydroglucose units that divide to alpha-cellulose, beta-cellulose and gamma-cellulose on the base of its degree of polymerization. In general, the alpha-cellulose indicates an undegraded, higher-molecular-weight cellulose content in pulp; the beta-cellulose indicates a degraded cellulose, and the gamma-cellulose consists mainly of hemicellulose [15,16].

In order to determine and compare the amount of degradation of cellulose, these components can be investigated by a different way. In acidic and alkaline pulping condition some degradation in cellulose is occurred. The acidic hydrolysis of glycosidic bonds of cellulose is of importance in many technical processes. The predominant degradation reaction in alkaline condition is the peeling reaction that by means of this mechanism some glucose units are removed from cellulose molecule and decreases its degree of polymerizeation (DP).

In general, organosolv pulping has low effect on carbohydrate degradation and has good selectivity in the delignification reaction. By protic solvents, such as alcohols, in the absence of acids and bases the main reactions occurred in the pulping process are hydrolyses and to a lower extent solvolysis. In the condition of aprotic DMF solvent, the main and only delignification reaction is hydrolysis.

By this reaction the carbohydrate-lignin etheric linkage is broken and α-O-4 and β-O-4 bonds of lignin molecules subjected to some hydrolysis and small fragments of lignin are formed. These fragments can be dissolved in solvent system. Thus, the aprotic solvent, DMF, has not any direct effect in delignification reaction, but a protecting effect to cellulose degradation by hydrolysis.

The quality of organosolv pulps is not competitive with the quality of corresponding Kraft pulps. Particularly in alcohol pulping, the pulp quality can be improved by adding alkali to the system. Although, some new solvents such as DMF have shown interesting results that pulping by them have many advantages such as obtained pulp with more hemicellulose, less cellulose degradation, high yield, low residual lignin content, high brightness, and good strength [7]. The pulp

produced is easy to bleach and the yield after bleaching is sometime higher than the yield of Kraft pulp.

Pulping processes have been modelled in many ways in order to derive equations for estimating the quality of the resulting pulp as a function of the process variables and optimizing the operating conditions. In this work, we used a central composition design to study the influence of cooking variables for wheat straw with dimethylformamide-water mixtures (viz: the cooking time, temperature, and the organic solvent concentration) on the various properties.

The tested model uses a series of points (experiments) around a central one (central experiment), and several additional points (additional experiments) to estimate the first- and second-order interaction terms of a polynomial. This design meets the general requirement that every parameter in the mathematical model can be estimated from a fairly small number of experiments [17].

So far, few authors have used a factor design to develop empirical models involving several independent variables to identify patterns of variation in the dependent variables (chemical composition, yield, residual lignin and degree of polymerization) of various pulping processes as applied to diverse vegetable materials. Organosolv pulping has been studied in this respect by many researchers [2, 5, 8, 10, 11, 18, 19, and 20].

In the present work, the wheat straw was pulped by DMF- water solvent system and the effect of DMF on the degradation of cellulose was evaluated by measurement of viscosity, α-, β-, and γ-cellulose contents, degree of polymerization (DP), and SEM observations.

EXPERIMENTAL

Raw Material

The wheat (Triticum vulgaris) straw used in this study has been obtained from the local wheat field in central of Iran. Before pulping, the raw material was cleaned, cut sample into pieces of approximately 3 cm length and sun-dried. The chemical composition of wheat straw was determined as follows: 51.53% cellulose, 18.29% lignin, 72.27% holocellulose, 44.05% α-cellulose, 7.57% ash and, 1.57% ethanol/dichloromethane

extractable on an oven-dry weight basis (moisture content 9.8%). The deviations of these contents from their respective means were all less then 10%.

In this research dimethylformamide was selected for delignification of wheat straw as solvent with medium boiling point (152-154ºC) that in high cooking temperature (210ºC), the maximum pressure generated was 12 atm. The chemical solvent (dimethylformamide) may be considered as an environment for solubilizing fragmentation products of lignin that is produced by thermo-hydrolysis reaction.

Methods of Analysis of Raw Material and Pulps

Analysis of raw material and pulp of wheat straw made according to Tappi Standard Methods [21] with the exception of hemicellulose that determined by decreasing of cellulose content from holocellulose (holocellulose determined by Wise's sodium chlorite method)[22], cellulose according to Kurscher and Hoffner's nitric acid method [23] and viscosity of pulp was measured in cupri-ethylenediamine (CED) solution according to SCAN-CM 15:88 standard and DP (degree of polymerization of cellulose) was calculated by eqn (12). Pulp yield was determined gravimetrically following the drying stage at 105 ±2°C after 24 h.

Experimental Design
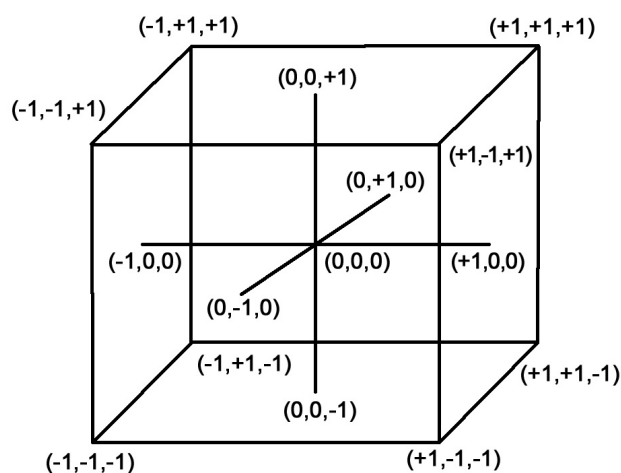
The tested model in Figure 1 uses a series of points

Figure 1. Plot of coordinates for the experiments included in the experimental design, based on three independent variables.

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(experiments) around a central one (central experiment) and several additional points (additional experiments) to estimate the first- and second-order interaction terms of a polynomial. This design meets the general requirement that every parameter in the mathematical model can be estimated from a fairly small number of experiments [17].

The total number of observations (experiments) required for the three independent variables (viz. temperature, T, cooking time, t, and dimethylformamide-water mixture, D) were calculated by the following equation [25]

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

and found to be 15. In the equation, k is the number of independent variables.

In this work, all independent variables, i.e., temperature, DMF concentration, and cooking time) normalized from -1 to +1 according to following formula [3]

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

This normalization also results in more accurate estimates of the regression coefficients as it reduces interrelationships between linear and quadratic terms [17]. The normalized independent variables and experimental data of properties of the pulp were used for the development of empirical models, in which the dependent variables were evaluated by the following general equation:

$$Z = a + bX_T + cX_t + dX_D + eX_T^2 + fX_t^2 + gX_D^2 + \\ hX_TX_t + iX_TX_D + jX_tX_D \qquad (3)$$

Where Z denotes the response variables (C: cellulose content, α-C: α-cellulose, γ-C: γ-cellulose, H: hemicellulose, RL: residual lignin, YI: yield, SCAN viscosity and DP: degree of polymerization of pulp, X_T, X_t and X_D are the normalized values of T, t and D and coefficents a-j are constants.

The values of responses obtained allow the calculation of mathematical estimation models for each response, which were subsequently used to characterize the nature of the response surface.

Pulping

Pulps were made in a 21-l batch cylindrical mini-digester (stainless steel 321). The mini- digester includes an electrical heater, a motor actuator and required instruments for measurement and control of pressure and temperature. In a typical experiment, 300 g of oven-dried wheat straw (moisture content 9.8%) was weighed and charged into the mini digester. The solid/liquor ratio was fixed (1/12 dry per water). And the dimethylformamide-water mixture in the cooking liquor was set 30%, 50%, 70% by weight. After the mini-digester was loaded with wheat straw and the cooking liquor, it was heated to the operating temperature, which was then maintained throughout the experiment.

After cooking process, the cooked pulp was then washed with warm water and, finally disintegrated (with 3000 rpm and 2.5 min) in a standard disintegrator (T 205 sp-95). Afterward, the pulps were beaten in a stainless steel PFI mill under standard conditions (T 248 sp-00). The temperature, pulping time and dimethyl-formamide-water mixture used in the different experiments of the CCD were 190, 200 and 210°C, 120, 150 and 180 min and 30/70 (or 30%), 50/50 (or 50%) and 70/30 (or 70%) by weight, respectively. In order to obtain more precise and acceptable experimental data, the cooking of wheat straw was reproduced in three reiteration and the properties of all of them were measured carefully. Also, in the other part of this work, some Kraft pulp of wheat straw was made in order to compare the effect of Kraft with organic solvent on pulp properties.

Response Surface Analysis of Organosolv Pulping
The multiple non-linear regression analysis was performed on all the terms of eqn (3), by MINITAB software (version 14) (by using data in Table 1). The coefficients of dependent variables derived according to the eqn (3) are given in Table 2.

On the basis of the experimental results, the cooking operation conditions in the optimization process were changed over the following ranges:

Cooking time: 120-180 min

Cooking temperature: 190-210ºC

DMF concentration: 30-70% at constant ratio of 12:1 for liquid to dry weight of wheat straw.

The MINITAB software suite was used to conduct a multiple linear regression analysis involving all the

Table 1. Values of the independent variables properties of the pulp obtained in the pulping process by using the proposed experimental design.*

Cooking No.	X_T	X_t	X_D	T (ºC)	t (min)	D (%)	C (%)	α-C (%)	γ-C (%)	H (%)	YI (%)	Residual lignin (%)	SCAN viscosity (cm³/g)	DP
1	+1	+1	+1	210	180	70	64.96	75.08	10.71	8.94	52.64	5.01	1255	4021
2	+1	-1	+1	210	120	70	69.26	75.29	11.97	11.18	53.01	5.73	1330	4358
3	-1	-1	+1	190	120	70	65.66	71.82	24.11	3.20	66.56	10.88	–	–
4	-1	+1	+1	190	180	70	69.03	72.98	19.53	3.71	64.45	8.08	1341	4406
5	-1	+1	-1	190	180	30	64.61	76.18	12.96	7.01	57.36	7.79	1304	4247
6	+1	+1	-1	210	180	30	65.73	82.59	9.26	8.62	50.33	5.88	1248	4008
7	+1	-1	-1	210	120	30	67.17	78.99	8.98	6.87	51.10	6.91	1269	4097
8	-1	-1	-1	190	120	30	69.21	73.16	15.28	6.59	57.90	9.26	–	–
9	0	0	0	200	150	50	71.04	77.04	9.38	14.28	57.00	6.76	1285	4165
10	0	+1	0	200	180	50	68.01	79.26	12.09	9.52	55.15	6.61	1269	4097
11	+1	0	0	210	150	50	69.33	84.13	7.93	7.82	53.05	6.17	1264	4076
12	0	-1	0	200	120	50	68.04	76.22	10.50	8.98	55.89	7.35	1334	4376
13	-1	0	0	190	150	50	64.70	73.01	10.96	12.57	60.90	7.64	1343	4415
14	0	0	+1	200	150	70	62.60	73.92	11.56	13.94	60.00	6.61	1294	4207
15	0	0	-1	200	150	30	62.87	75.52	13.80	9.92	54.45	6.76	1281	4148

(*)X_T: normalized temperature; X_t: normalized cooking time; X_D: normalized dimethyl formamide water mixture; C: cellulose; α-C: α-cellulose; γ-C: γ-cellulose; H: hemicellulose; RL: residual lignin; YI: yield (value referred to pulping process); SCAN viscosity: viscosity of pulp; DP: degree of polymerization.

terms of eqn (2) except those with alpha-to enter 0.15 and alpha-to remove 0.15, which were left out using the stepwise method [26]. The following eqns (4)-(11), are reduced models for each response:

$$\text{Cellulose} = 67.39 + 2.1X_t^2 - 3.2X_D^2 + 1.30X_T X_t \quad (4)$$

$$\alpha\text{-Cellulose} = 78.03 + 2.89X_T + 1.1X_t - 1.74X_D - 2.5X_D^2 \quad (5)$$

$$\gamma\text{-Celluloses} = 10.17 - 3.40X_T + 1.76X_D + 3.6X_D^2 - 1.37X_T X_D \quad (6)$$

$$\text{Hemicelluloses} = 12.69 - 2.4X_D - 3.3X_T^2 + 1.42X_T X_D \quad (7)$$

$$\text{Residual lignin} = 6.79 - 1.4X_T - 0.68X_t + 0.56X_t^2 - 0.50X_T X_D \quad (8)$$

$$\text{Yield of cooking} = 56.60 - 4.79X_T - 0.45X_t + 2.55X_D - 1.44X_T X_D \quad (9)$$

$$\text{SCAN viscosity} = 1288 - 38.6X_T - 28.6X_t + 16.5X_D + 13.7X_T^2 + 11.7X_t^2 \quad (10)$$

$$\text{DP} = 4178 - 165X_T - 120X_t + 71X_D + 59X_T^2 + 50X_t^2 - 38X_t X_D \quad (11)$$

The stepwise forward selection method also includes statistics that can be used for model selection. The statistics include:

P-Value: For the data of project, alpha-to enter is 0.15, thus at each step of procedure, a predictor is added to the model if it has the smallest P-value among those predictors with P-value less than 0.15.

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Table 2. Coefficients of the equations that relate the dependent and independent variables, S values, R-sq values, R-sq (adj), and Mallow C-p

Coefficient equations and values of analysis regression	Equation: $Z = a + bX_T + cX_t + dX_D + eX_T^2 + fX_t^2 + gX_D^2 + hX_TX_t + iX_TX_D + jX_tX_D$							
	Cellulose eqn(4)	α-Cellulose eqn(5)	γ-Cellulose eqn(6)	Hemicellulose eqn(7)	Residual lignin eqn(8)	YI eqn(9)	SCAN viscosity eqn(10)	DP eqn(11)
a	67.39	78.03	10.17	12.65	6.79	56.60	1288	4178
b	–	2.89	-3.40	–	-1.4	-4.79	-38.6	-165
c	–	1.1	–	–	-0.68	-0.45	-28.6	-120
d	–	-1.74	1.76	-2.4	–	2.55	16.5	71
e	–	–	–	16.5	–	–	13.7	59
f	2.1	–	–	–	–	–	–	–
g	-3.2	-2.5	3.6	–	–	–	–	–
h	1.30	–	–	–	–	–	–	–
i	–	–	-1.37	1.42	-0.50	-1.44	–	–
j	–	–	–	–	–	–	–	-38
S	2.14	1.86	2.29	2.27	0.55	0.7	10.6	45.5
R-sq	45.47	80.96	79.73	61.84	90.05	98.46	95.21	95.16
R-sq (adj)	30.60	73.34	71.62	51.43	86.07	97.84	90.41	90.32
Mallows C-p	0.7	3.6	2.4	0.3	3.0	11.6	5.4	5.5
P-Value	0.133	0.099	0.121	0.11	0.103	0.068	0.116	0.102

S: an estimate of the standard deviation of the error term in model. In general, the smaller the S, the better the model fits the data.

R-sq: the proportion of the variation in the response data explained by the model.

R-sq (adj): a modified version of the R that has been adjusted for the number of predictors in the model. In general, the larger the R, R (adj), the better the model fits the data.

Mallow C-p: another statistics for assessing how well the model fits the data. C-p should be close to the number of predictors contained in the model.

Some of the statistical analysis such as P-Value, R-sq, R-sq (adj), Mallow C-p and S are summarized in Table 2 and the results confirm the adequacy of the fitted models, where all models with the exception for, α-cellulose, γ-cellulose, residual lignin, yield of cooking, SCAN viscosity and DP are R-sq at a level of 75 or more. Also the coefficient estimates for each term in the selected models are shown for every dependent variable.

The steepest ascent method [27] was applied to eqns (4)-(11) in order to determine the highest properties over the ranges of process variables studied (normalized values from -1 to +1 for all). These equations allow the estima-tion of the variation of the properties of the pulp with changes in each independent variable to be consistent with the other two variables over the range considered.

RESULTS AND DISCUSSION

Cellulose Content

Cellulose is a glucan polymer of D-glucopyranose units, which are linked together by β-(1-4)- glucosidic bonds. Actually the building block of cellulose is cellubiose since the repeating unit in cellulose is two sugar units. However, it seems that DMF as an organosolv solvent has the main effect on cellulose percentage in the obtained pulps. The reason of higher role of DMF is related to this fact that hydrolytic reactions and cellulose chain degradation were reduced by increasing of DMF ratio (or the water charge as an affective parameter in the hydrating reaction has been decreased).

A response surface graph showing in the cooking time and DMF ratio on cellulose at 210ºC is presented in Figure 2. It should be noted that, in Figure 2 there is an optimum region (maximum cellulose value) at high temperature and middle cooking time and DMF ratio.

Table 3. Optimum (maximum) values of dependent variables and variations with changes in the independent variables in the DMF pulping and handsheet making of wheat straw.

Variables dependent	Error percentage[a]	Optimum values	Normalized values[b]			Maximum changes[c]		
			X_T	X_t	X_D	T	t	D
Cellulose	5.28%	67.39	0	0	0	−	3.1 (4.7%)	2.12 (3.12%)
α-Cellulose	3.75%	80.97	+1	0	0	5.78 (7.14%)	1.11 (1.37%)	4.24 (5.24%)
γ-Cellulose	15.8%	20.3	-1	-1	+1	9.54 (47%)	−	6.73 (33.15%)
Hemicellulose	11.41%	12.65	0	0	0	2.4 (18.97%)	3.3 (26.08%)	
Residual lignin	8.73%	9.93	-1	-1	+1	3.8 (38.27%)	1.36 (13.7%)	1 (10.09%)
	4.79%(minimum)	4.77	+1	+1	+1	1.8 (37.95%)	0.505 (10.58%)	1 (20.96%)
Yield	-0.73%	65.83%	-1	-1	+1	12.46 (18.93%)	0.9 (1.37%)	8.07 (12.26%)
	1.13% Minimum)	50.25%	+1	+1	-1	6.7 (13.33%)	0.9 (1.79%)	2.22 (4.42%)
SCAN viscosity	−	1395	-1	-1	+1	75 (5.37%)	56 (4.01%)	31 (2.22%)
	1.12% Minimum)	1234	+1	+1	-1	75 (6.10%)	56 (4.55%)	31 (2.51%)
DP	0.97%(minimum)	3969	+1	+1	-1	330 (8.31%)	276 (6.95%)	218 (5.49%)

(a) Error percentage of the experimental values with respect to optimum values, (b)Normalized values of the independent variables leading to optimum values of the dependent variables, (c) Maximum changes in the dependent variables (in units and percentages with respect to the optimum values, which are shown in brackets) with change in the independent variables.

Although the maximum cellulose value has been obtained in this region, but this situation can not be accepted because increasing the cellulose content alone do not help to improve the properties of pulp products.

However, because of low value of R-sq of this equation (45.47), it can be understood, there are other influential factors on this characteristic that cause to increase the error percentage of the experimental values with respect to optimum values.
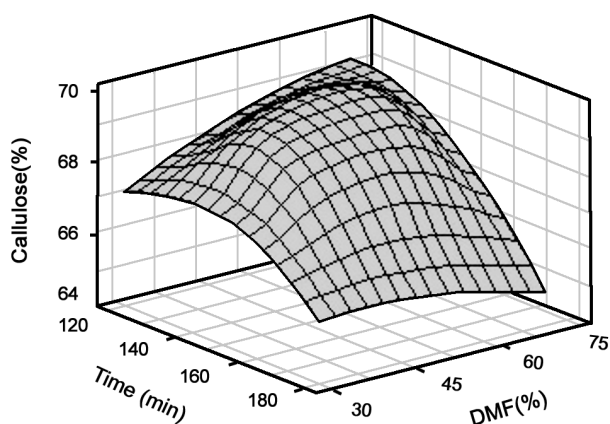
α-Cellulose

α-Cellulose is the main part of cellulose which its chains are built up of more than 150 units. It was applied and considered as an important factor to investigate the quality of obtained pulp [28]. Statistical analysis shows that of three factors affecting α-cellulose, the most effective factor is cooking temperature (7.14%), followed by DMF ratio (5.24%), while the cooking time is the least effective factor (1.37%), (Table 3). As the same
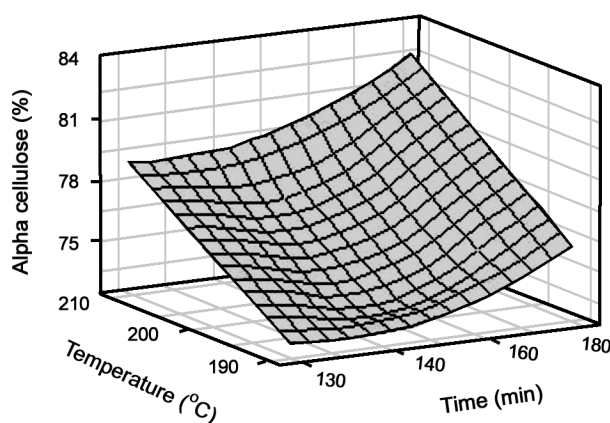

Figure 2. Variation of pulp cellulose with cooking time and DMF ratio at a high constant temperature.

Figure 3. Variation of alpha cellulose content with temperature and cooking time at a low constant DMF ratio.

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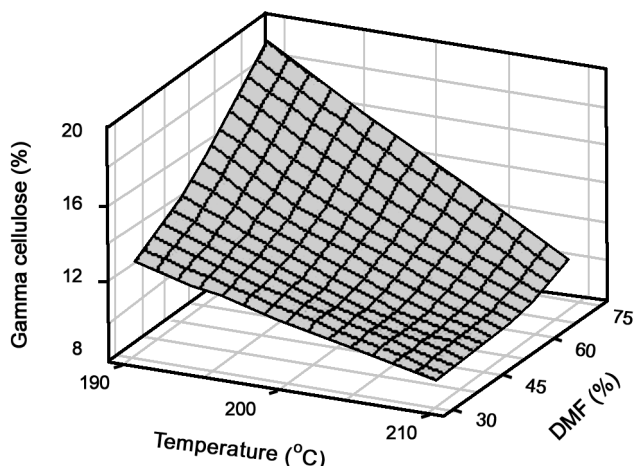Study on Cellulose Degradation during Organosolv...   Ziaei-Shirkolaee Y. et al.

Figure 4. Variation of Gamma cellulose with temperature and DMF ratio at a long constant cooking time.

Figure 5. Variation of hemicellulose with cooking time and DMF ratio at a high constant temperature.

way according to eqn (5), it can be seen that the coefficient of DMF ratio (1.74) is less than the temperature coefficient (2.89). The effects of temperature and time at low DMF ratio are presented in Figure 3. It indicates that at low DMF ratio, by increasing the temperature and time, the α-celluloses content increases. In addition, similar to statistical analysis, the effect of cooking temperature on α-celluloses percentage is higher than the effect of cooking time.

γ -*Cellulose*

γ-Celluloses include hydrocarbon chains with 15 units or less [28]. The effects of cooking temperature, cooking time and DMF ratio on γ-cellulose values are given in Tables (1), and (3) and eqn (6). Statistical analysis shows that of three factors affecting γ-cellulose, variation of cooking temperature showed the most significant effect (47%) followed by DMF ratio (33.15%), while the cooking time has no significant effect. Also it seems that in the region of constant time elapsed, increasing the DMF ratio has positive effect in comparison with cooking temperature (Figure 4). At low level of cooking temperature, according to Figure 4, the DMF ratio has a high impact on obtained -celluloses in comparison with its effect at high level of cooking temperature. On the other hand, cooking temperature has a strong effect on obtained γ-celluloses at high level of DMF ratio in comparison to its effect at low level of DMF ratio.

Based on eqns 5 and 6, it can be understood that DMF plays a complementary role on the variation of α- and γ-cellulose from a statistical standpoint. Since DMF has
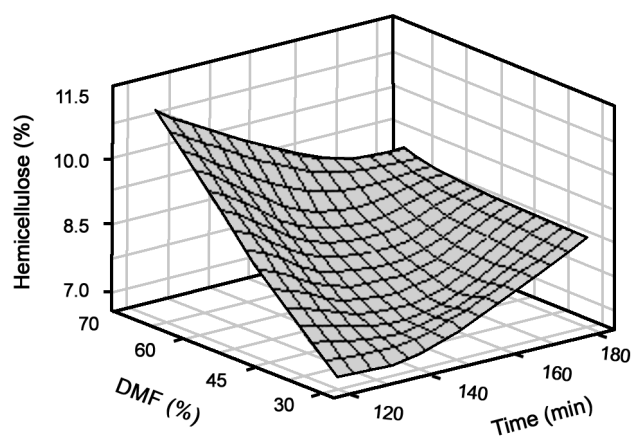
significant effects (1.76, 3.6) on γ-celluloses, by temperature increase, there would be a negative interaction effect (1.37) between temperature and DMF, despite the fact that DMF has negative effect on α-cellulose as well. This means that by the increase in γ-cellulose, the percentage of α-cellulose decreases automatically.

Hemicelluloses

In general, the hemicelluloses fraction in plants consists of a collection of polysaccharide polymers with a lower DP than cellulose and containing mainly the sugars D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amounts of other sugars [29]. They usually contain a backbone consisting of one repeating sugar unit linked β-(1-4) with branch points (1-2), (1-3), and/or (1-6). The retention of polysaccharides (particularly hemicelluloses) during delignification or bleaching of pulp has a critical influence on yield and papermaking properties of pulp [12]. It is evident that the results of hemicelluloses are less in compared with cellulose (Table 1). The statistical analysis shows that there is a positive interaction (1.42) between temperature and DMF ratio according to eqn (7).

As can be seen in Table 3 and according to eqn (7), statistical analyses of the interaction effects of the pulping variables show that the DMF concentration and cooking temperature have significant effects on keeping hemicellulose during the increasing of pulping time. With constant temperature, time, and DMF concentration at their normalized values (of 0) the greatest
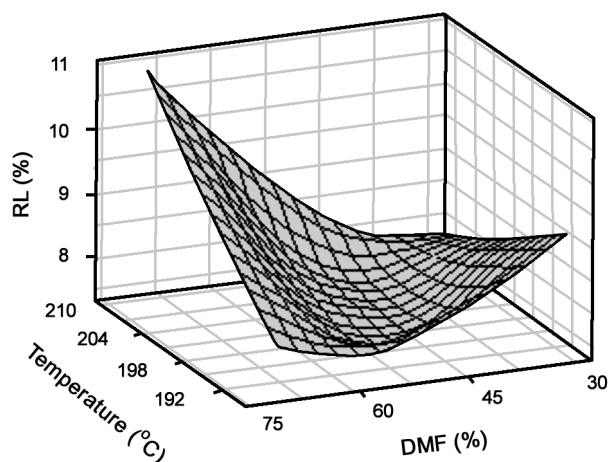
Figure 6. Variation of Residual lignin with cooking time and DMF ratio at a low constant temperature.

Figure 7. Variation of pulp yield with cooking time and DMF ratio at a low constant temperature.

changes in hemicellulose are resulted from variation of the time (3.3 units or 26.08% with respect to the maximum value) while the processing DMF concentration has directly insignificant effect on the hemicellulose.

As is shown in Figure 5, at high level of constant temperature, by increasing the DMF ratio, hemicelluloses content increases rapidly. In the same way, by synchronous rising of DMF ratio and cooking time, hemicellulose content increases slowly. This result points on the low hydrocarbon degradation during short cooking time and in duration of process, the role of organic solvent (DMF) has been more significant in reducing the degradation by raising the concentration.

Residual Lignin
Lignin is a third macromolecular biofibres materials component. The molecules of lignin are built up quite differently from polysaccharides, as they consist of aromatic system composed of phenyl propane units. There is less lignin in non woods than woods materials and in most cases of biofibres utilizations lignin is used as an integrated part of biofibres. There are a variety of puling processes for delignification but, it is not possible to removed lignin totally by selectivity methods. However, it seems that delignification process can be applied by use of DMF as an organosolv solvent with high percentage of selectivity.

The principal effects of temperature, time and DMF ratio on residual lignin are shown in Tables 1 and 3 and eqn (8). It should be noted that the variation of temperature had the highest effect (38.27%) on reducing the
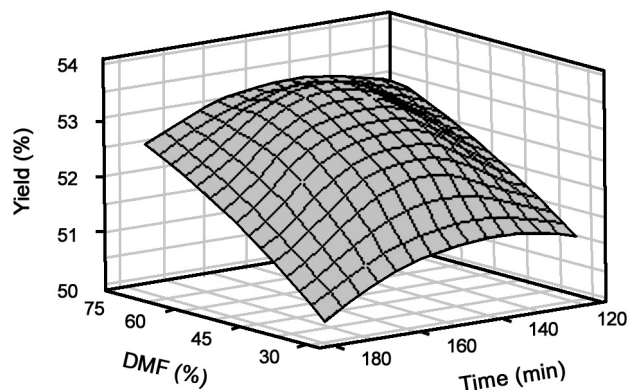
lignin in pulp at all levels of cooking time and DMF ratio conditions. At highest level of residual lignin, it was much more sensitive to changes in time (13.70%) more than in DMF ratio (10.09%), but at smallest one, the effect of DMF ratio (20.96%) was higher than time factor (10.58%). The response of residual lignin to DMF ratio and cooking time at low temperature are illustrated in Figure 6. According to Figure 6, the effect of DMF ratio is decreasing when cooking time increases at constant level of cooking temperature.

Yield of Cooking
Eqn (9) was used in order to determine the maximum yield over the ranges of process variables studied (normalized values from -1 to +1 for all); the maximum yield calculated for a low temperature and a short time (a normalized value of 1 for both variables), in addition to a high DMF ratio (normalized value +1) was 65.83%. The yield was much more sensitive to changes in temperature than in the DMF ratio and time and the greatest changes in yield are resulted from variations in the temperature (12.46 units or 18.93% with respect to the maximum value) and the smallest ones from variations in the processing time (0.9 units or 1.37%). The effect of the pulping DMF ratio was (8.07 units or 12.26 %). These results are confirmed by Figure 7.

From the foregoing analysis it follows that, by a medium ratio of DMF, in addition to a low, suitable temperature and a medium time, the yield decreases to 61.39%, i.e., by only 4.44% with respect to its highest level (65.83%). Also in a normalized value of -1 for all

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Table 4. Kraft pulping conditions* (for obtained kappa number).

Time at maximum temperature (min)	Sulphide (%)	Active alkali (NaO$_2$%)	Yield (%)	Residual lignin (%)	SCAN viscosity (cm³/g)
30	20	14	43	6.60	1095
40	20	14	40.5	6.17	992
30	20	16	41.2	5.73	998
50	20	16	40.1	5.01	910

(*) constant temperature: 160 ºC and time to maximum temperature : 60 min

of variables, yield decreases to 57.85 %, i.e., by only 7.98% with respect to its maximum level, but by substantial savings of cooking solvent. Because, in the operations of recovering and recycling some loss is always inevitable.

On the basis of the previous study on Kraft pulping of wheat straw [30], in order to obtain similar residual lignin content of DMF pulp, the cooking conditions are given in Table 4. The obtained results show that the yields of organosolv pulping have been almost higher than those of Kraft pulping. The protective action of organosolv on non-cellulosic polysaccharides of wheat straw against degradation under Kraft pulping conditions was mentioned as a main reason of the fairly high yield of organosolv pulps [12].

Cellulose Degradation Based on SCAN Viscosity
The advantages of this solvent in comparison with other pulping processes include more retention of carbohydrates and low degradation of cellulose (assessed by the yield and viscosity in comparison with other processes). The use of increasing DMF ratio had a very significant

effect on reducing cellulose degradation that means the viscosity of pulps were increased with increasing DMF ratio under mild cooking condition. The results of viscosity can be applied in estimating the extent of cellulose degradation during cooking process [24]. The main effect of temperature, DMF ratio and cooking time on SCAN viscosity are shown in Table 3 and eqn (10). Because of high amount of residual lignin, there is not possible to measure SCAN viscosity in condition of (-1,
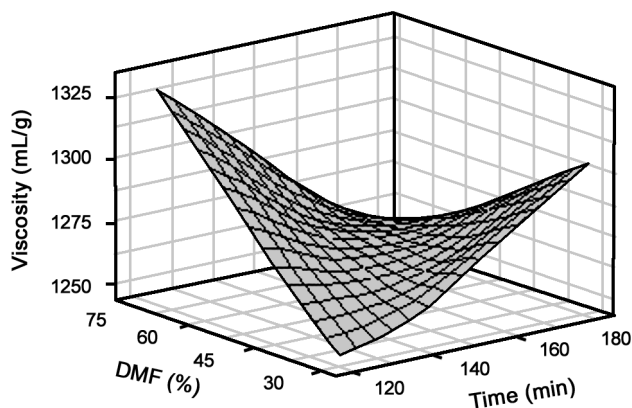

Figure 9(a): Viscosity (mL/g) = 1116+29.91 R.L -0.520 RL^2

S   26.0391
R-Sq   63.5%
R-Sq (adj) 57.4%

Figure 9(b): Viscosity (mL/g) = 712+14.09 Yield -0.0643 Yield^2

S   26.3777
R-Sq   62.5%
R-Sq (adj) 56.3%

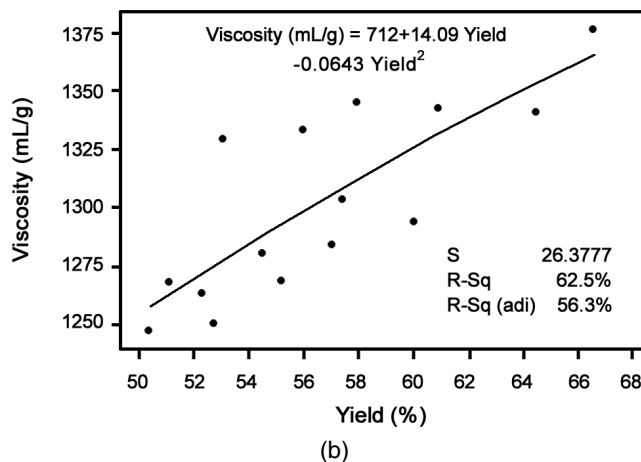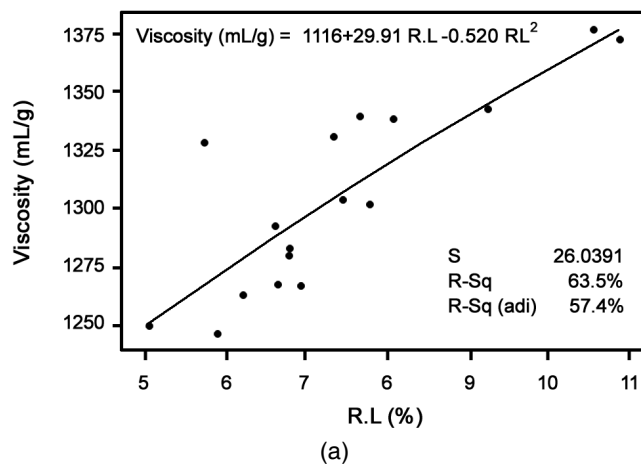**Figure 8.** Variation of pulp SCAN viscosity with cooking time and at DMF ratio a high constant temperature.

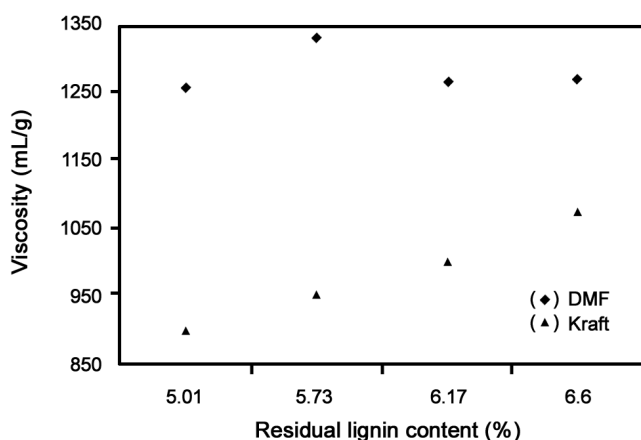**Figure 9.** The SCAN viscosity as: (a) function of residual lignin and (b) function of yield.

Figure 10. Delignification selectivity of organosolv pulping (DMF) in comparison with kraft pulping.

-1, +1) and (-1, -1, -1). The error percentage of the experimental viscosity values with respect to values of the equation was negligible. That means the highest error of percentage of viscosity obtained just 1.2% according to eqn (10).

It is apparent that the cooking temperature was the most influential factor in relation to the viscosity of wheat straw pulp at all levels of cooking temperature (75 units), followed by the cooking time, (56 units) at maximum and minimum viscosity. The effect of increasing DMF ratio on viscosity was weak at high levels of temperature and cooking time while, this factor was greatly affected in low surface of cooking time (Figure 8).

In general, the viscosity is a function of cellulose fibre degradation in pulping processes [24]. It is interesting to observe that cooking temperature was the main driving force for damaging of cellulose structure of wheat straw pulp on the basis of decreasing of the related viscosity in comparison with the two another main factors. In the same way maximum viscosity obtained at low levels of cooking temperature and cooking time plus high level of DMF ratio similar to condition of obtained maximum values of yield and residual lignin (Figures 9 a and 9 b).

In order to compare the effect of DMF with Kraft process on reducing the cellulose degradation of wheat straw, according to results of Table 4, there is a great difference between their amounts of viscosities that can be attained. Thus, DMF has basically improvement role on reducing the cellulose degradation. This phenomenon can be strongly used to improve of pulp production that

(a)

(b)

Figure 11. SEM Photographs of wheat straw pulp at (kappa number~39): (a) Kraft process; (b) organosolv (DMF) process.

is very important in related industries.

Delignification Selectivity
The change in pulp viscosity with lignin removal during organosolv cooking can be considered as a measure of delignification selectivity. In Figure 10, the SCAN viscosity of organosolv pulp from wheat straw cooking measured is shown as a function of residual lignin content. It is apparent that the delignification selectivity of DMF pulping is higher than Kraft pulping. A viscosity loss of only 5.7% was detected, where the viscosity drop of 16.5% was noted at the end of Kraft cooking.

Photographs of the pulps prepared by DMF and Kraft processes (taken by scanning electron microscopy technique) are shown in Figures 11 and 12. The fibres of the pulps in these photographs are smooth and clean.
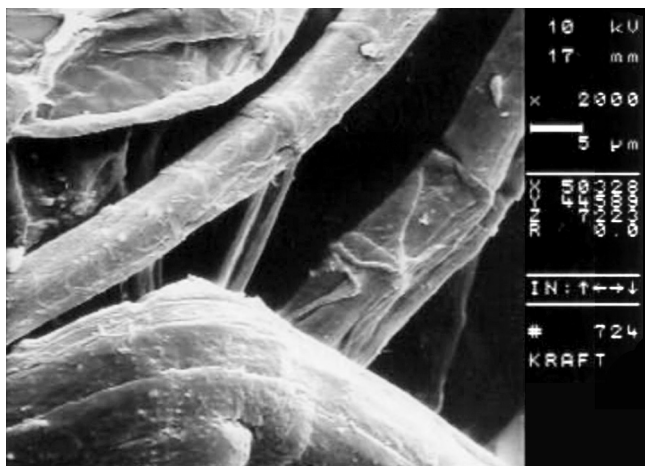
(a)
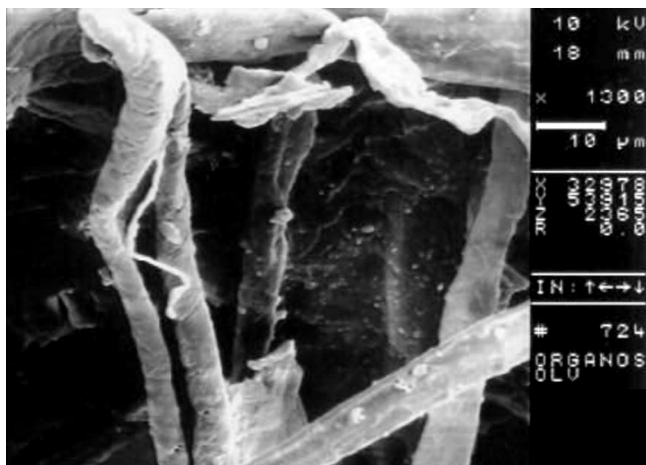
(b)

Figure 12. SEM Photographs of wheat straw pulp at (kappa number~46): (a) Kraft process; (b) organosolv (DMF) process.

These samples show fibrillation but they posses fibres of different thickness. As photographes 11a and 12a are compared with photograph 11b and 12 b, it can be seen that the Kraft pulps have higher thickness and lower flexibility. But fibres of pulps by DMF are softer and thinner than Kraft pulps which can be resulted from low degradation of holocellulose.

Degree of Polymerization

Degree of polymerization (DP) of cellulose was calculated by eqn (12) [10, 25]

$$DP^{0.76} = (SCAN\ viscosity)/2.28 \qquad (12)$$

Therefore, the principal effects of three parameters on DP are similar to viscosity variations (Table 3 and eqn (11)). It is apparent that the cooking temperature and time have high negative effects on DP. The effect of DMF concentration was comparatively positive which means by increasing the use of DMF, The degradation of cellulose would reduce. It can be said that DMF cause the damage of cellulose to decrease during the cooking process. Statistical analyses of the interaction effects of the pulping variables show that none of the variables has any significant interaction with other variables. But, they have the significant effect on DP.

CONCLUSION

In general, the advantages of pulping by DMF are generating a middle pressure in digester, more retention of carbohydrates, and low degradation of them [31]. By considering all obtained results, DMF has a significant effect on reducing carbohydrates degradation during cooking period especially on the basis of yield and DP. Even at all range of cooking temperature and time by increasing the DMF ratio, the yield of pulping improves. Thus, it can be resulted that cellulose degradation is being reduced during organosolv delignification of wheat straw by hydrolysis reaction in the aprotic condition of DMF solvent. According to experimental and statistical results, we can obtain optimum conditions of temperature: 200°C, DMF ratio: 50%, and cooking time: 150 min for producing a pulp with acceptable properties. Analysis of results reveals that, pulps obtained at 210°C, 180 min and 70% DMF ratio have a low residual lignin (kappa ~34) which indicates that the desired properties of the final product dictated the optimized pulping conditions. In the aprotic condition of DMF solvent, the main and only delignification reaction is hydrolysis.

ACKNOWLEDGEMENTS

ABBREVIATIONS

CCD: Central composite design

DMF: Dimethyl formamide
DP: Degradation of polymerization
RL: Residual lignin
SCAN viscosity: Scandinavian viscosity

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