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INFLUENCE OF RICE STRAW COOKING CONDITIONS ON PULP PROPERTIES IN THE SODA AQUEOUS ETHANOL PULPING

Shahram Navaee – Ardeh, Pedram Fatehi

Asian Institute of Technology, Pulp and Paper Technology, P.O. Box 4,
Klong Luang, Pathumthani 12120, Thailand

ABSTRACT

An experimental normalized design was used to examine the influence of independent variables (alcohol concentration, cooking time and temperature) in the soda aqueous ethanol pulping of rice straw on various produced pulp properties (cooking yield, kappa number, ash content, and α-cellulose content of pulp). Equation of each dependent variable as a function of independent variables using multiple nonlinear regression via MATLAB software (version 6.1) was fitted with high confidence level. Independent variables; ethanol concentration, cooking time and temperature varied over the ranges of 40-65 (%w/w), 150-180 min and 195- 210 ^{o}C, respectively. Response surface plots of the dependent variables versus the independent variables were considered. The results of experimental normalized design illustrated well fitting between model and experimental data. The acceptable amount of α-cellulose was achieved at 150 min cooking time, 210 ^{o}C cooking temperature and 65%w/w ethanol concentration. Large part of the pulping yield was allocated to the ash content of the pulp.

Keywords: experimental normalized design, rice straw, soda aqueous ethanol pulping, pulp properties, multiple nonlinear regression.

1 INTRODUCTION

Non–wood raw materials account for 5-7% of the total pulp and paper production in the world (Jiménez et.al, 2001a). Non-wood based raw materials can be applied as an effective substitution forever decreasing of forest wood resources specially in the most Asian countries. Organosolv pulping process won't solve all the exist processing problems of chemical pulping process but it could complement the production of several certain raw materials and also could provide some appreciable environmental advantages such as easy beachability, lower odorous emission and lower mill size (Stockburger, 1993). Features such as low price, low toxicity and easy to recovery make ethanol very attractive as cooking liquor (Oliet et.al., 2000). One of the remarkable problems in rice straw pulping in alkaline conditions is dissolving of silica into the black liquor and subsequent difficulties in recovery of chemicals. While, due to applying organosolv pulping, the most amounts of silica remain in the produced pulp. So far, it is expected that the recovery of organic solvent will be easy. Nowadays, optimization is the most important issue for investigation and development of qualification of industrial processes. Modeling principles can be used in the pulping process for estimating and controlling of the quality of obtained pulps as a function of the cooking process variables (Jiménez et.al., 2000 and 2001b).

Moreover, modeling strategy allows developing of empirical models containing of several independent variables for examining on the pulping yield, ash content, kappa number, α-cellulose of pulp. These empirical models are preferred respect to the complex theoretical models which are comprised two or more independent variables. In spite of several studies on the non-wood organosolv pulping, few researches have been conducted on the pulping of rice straw by organic solvents and employing of normalized experimental design to develop empirical models involving independent variables.

In this study, rice straw was cooked with soda aqueous ethanol at high temperatures and high pressures. The effects of the cooking variables, i.e., cooking time, temperature and ethanol concentration were examined on the pulp properties; i.e., cooking yield, kappa number, ash percent and α-cellulose to establish the optimum operating pulping conditions for the process.

2 EXPERIMENTAL

2.1 Analysis of Raw Material

The stems of rice straw from northern Iran were used for the pulping process. The composition of the stems were measured and found including of 11.35 % ash, 30 % lignin and 58.65 % holocellulose.

2.2 Pulping

Pulps were made in a 21-liter batch cylindrical minidigester (stainless steel 321) equipped with an electrical heater, a motor actuator and required controller instruments (Navaee et.al, 2003). In a typical experiment, 300 g oven dry rice straw (moisture content 13.34%) was weighed and charged into the minidigester. The ratio of liquor to rice straw was 10:1 (o.d. basis) and the ethanol concentration in the cooking liquor was 65%w/w. The concentration of NaOH on the liquor was 1% oven dry basis of rice straw. The minidigester was then closed and simultaneously heated and actuated to assure good mixing and uniform swelling of the straw. The temperature was set to 100, 140 and 180 ºC at 30 min intervals for impregnation of liquor into the rice straw. The cooking process was followed by a further 180 min at 195ºC as cooking temperature. At the end of the cooking process, after turning off the heating system minidigester was discharged under ambient conditions. The pulp was washed with warm water. The washed pulp then was centrifuged, homogenized and then it was weighed. Dry matter content of pulp was determined according to the standard method given in Table 1 and cooking yield was calculated and followed by a screening process. Kappa number and the other pulp properties were measured according to the standards given in Table 1. The results of analysis of produced pulps and experimental cooking conditions have been summarized in Table 2.

Table1: Standards Employed for the Measurement of Raw Material and Produced Pulp Properties

Analysis	Method
Kappa Number	TAPPI T 236 cm-85
Ash (%)	TAPPI 211
α-Cellulose (%)	TAPPI 203 os-61
Pulp Dry Matter Content (%)	SCAN-C 3:78
Raw Material Dry Matter Content (%	SCAN-CM 39:94

2.3 Experimental Design Procedure

The experimental normalized design in the present study was done based on the normalized variables. In order to facilitate direct comparison of coefficients and better understanding of the effects of individual variables on the response variables, all of independent variables (temperature, ethanol concentration and cooking time) were normalized according to the following formula (Navaee et.al., 2004):

$$x_i = \frac{X_i - X_{\min}}{X_{\max} - X_{\min}} \quad (1)$$

The dimensionless independent variables and experimental data of pulping properties were used for the development of empirical models. Dependent variables (i.e., cooking yield, kappa number, ash percent, α-cellulose) were fitted according to the following generic formula as a function of independent variables (i.e., cooking temperature, ethanol concentration) (Montgomery, 2001):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 \quad (2)$$

Constant coefficients of Eq.(2) were obtained by fitting the experimental data given in the Table 2, using least square method via MATLAB software (version 6.1). This generic form of equation has been powered using interaction term through the main linear effects which is able to represent some curvature in the response function of pulping properties, i.e., cooking yield, α-cellulose, kappa number, ash content. Normalization of the independent variables also provides better estimation for the regression coefficients due to reducing correlation between linear and nonlinear interaction terms (Montgomery, 2001).

Table 2: Cooking Conditions (Independent Variables) and Experimental Results of Pulping Process Including Total Cooking Yield, Kappa Number, Ash Percent and α-Cellulose

t(*min*)	Ethanol concentration		Cooking temperature		*Y* (%)	*AP* (%)	*AC* (%)	*KN*
	C (% w/w)	x_c	*T(ºC)*	x_T				
150	40	0	200	0.304	56.5	69.19	79.8	85
150	45	0.2	199	0.26	57.28	72.18	78.1	82.5
150	50	0.4	210	1	52	66.16	80.5	51.6
150	60	0.8	196	0.174	61.77	70.9	76.3	55.4
150	65	1	196	0.174	60.38	64.8	78.5	64
180	40	0	200	0.304	50	60	79.2	83.4
180	45	0.2	210	1	54.21	66.54	77.8	75
180	50	0.4	195	0	61	73.9	82.8	72
180	60	0.8	199	0.26	58.8	72.37	71.75	87
180	65	1	200	0.304	57.33	67.48	73.65	104

3 RESULTS AND DISCUSSION

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

- Cooking time : 150- 180 min
- Cooking temperature : 195-210 ^{o}C
- Ethanol concentration: 40-65 % w/w at constant liquor to rice straw ratio (10:1).

The results of experimental design have been summarized in Table 3.

Table 3: Linear and Nonlinear Coefficients Yielded from the Experimental Normalized Design of Dependent Variables (Pulp Properties) According to Eq. (2)

Cooking time(min)	Dependent variable	β_0	β_1	β_2	β_{12}	r^2
150(short cooking time)	*Y* (%)	60.71	0.6605	-14.41	13.53	0.959
	AC (%)	69.55	14.9597	34.18	-73	0.855
	AP (%)	94.48	-45.861	-84.16	185.32	0.826
	KN	83.43	-11.108	9.02	-90.52	0.882
180 (long cooking time)	*Y* (%)	39.83	52.291	33.72	-149.4	0.993
	AC (%)	75.62	14.2343	13.66	-73.75	0.994
	AP (%)	44.32	74.6329	51.23	-219.3	0.994
	KN	117.3	-116.47	-110.12	453.55	0.982

As can be seen, for all the dependent variables, generally at long cooking time (180 min) there was high validity of model fitting with the experimental data. As it can be seen from Fig. 1, at low ethanol concentration the cooking yield was very sensitive to the changes of temperature but with increase of the ethanol concentration sensitivity of the cooking yield response decreased so that at 65% ethanol concentration there was not observed any significant change in the cooking yield when the temperature varied. Response of the cooking yield at low temperature versus ethanol concentration was negligible as well as at high ethanol concentration versus temperature.

At short cooking time (150 min), in both cases of high cooking temperature and ethanol concentration, the cooking yield was very sensitive to the changes of another independent variable (Fig. 1).

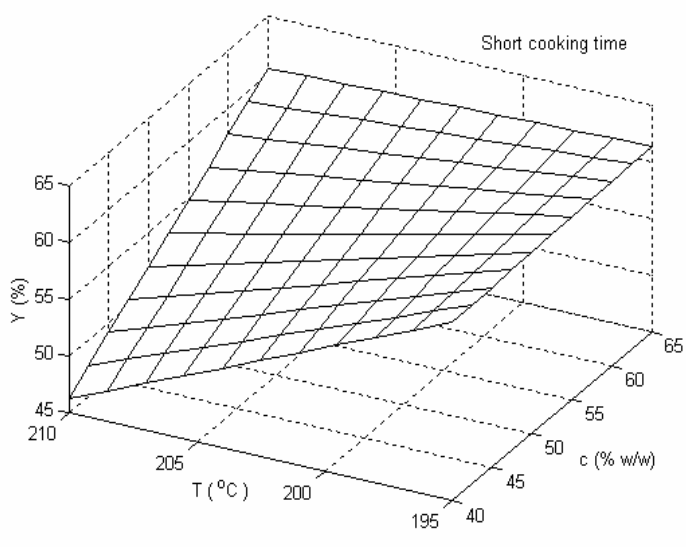

Figure 1: Variation of Cooking Yield vs. Cooking Temperature and Ethanol Concentration (150 min)

However in these cases both of kappa number (150 min) and α-cellulose (150 and 180 min) of the pulp were in the lowest value (Figs. 2 and 4), so the high value of cooking yield can be explained in term of high amount of ash content in this area which has been illustrated in Fig. 3 and Table 2.

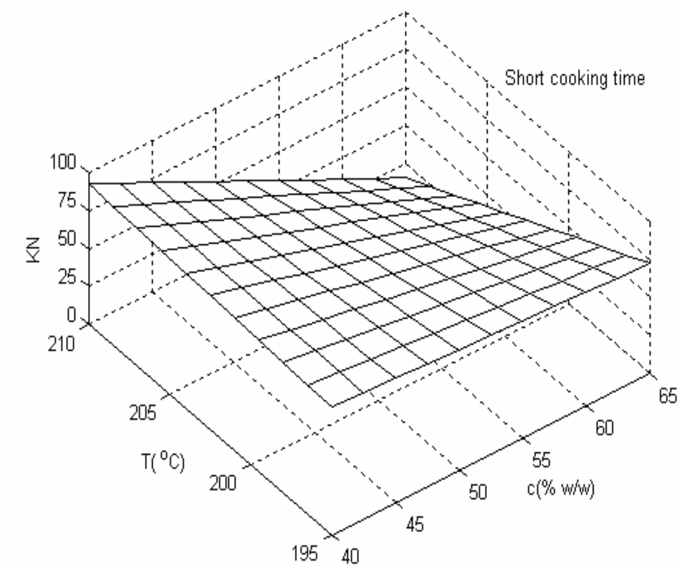

Figure 2: Variation of Kappa Number of Produced Pulp vs. Ethanol Concentration and Cooking Temperature (150 min)

Fig. 3 indicates high sensitivity of the ash content to the increase of cooking temperature at high ethanol concentration and vice versa. At low temperature, kappa number didn't change with increase of ethanol concentration. This trend was also observed at low ethanol concentration when temperature varied (Fig. 2).

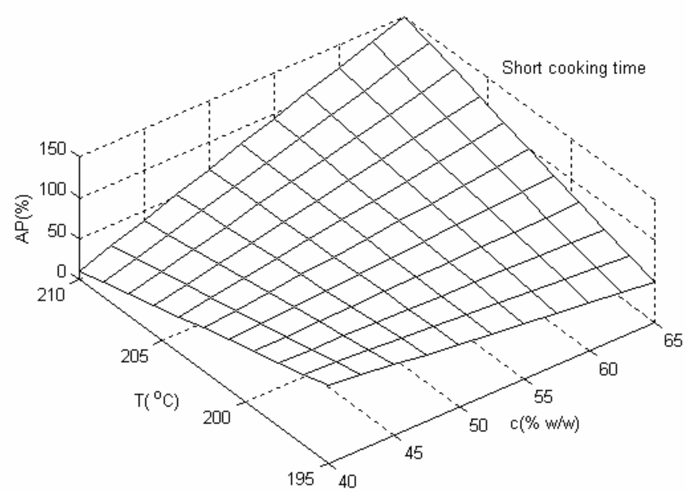

Figure 3: Variation of Ash Percent in Pulp vs. Ethanol Concentration and Cooking Temperature (150 min)

At long cooking time (180 min) and high ethanol concentration (65% w/w), there was a significant response for α-cellulose with increase of the temperature. The similar trend can be seen at high cooking temperature (210 °C) and time (180 min) when the ethanol concentration varied (Fig. 4). The response of α-cellulose to the temperature at low ethanol concentration (40% w/w) was negligible. Furthermore, the amount of α-cellulose was constant at low cooking temperature (195 °C) while the ethanol concentration was changing. As a result, the acceptable amount of α-cellulose of pulp was achieved at high temperature and high ethanol concentration.

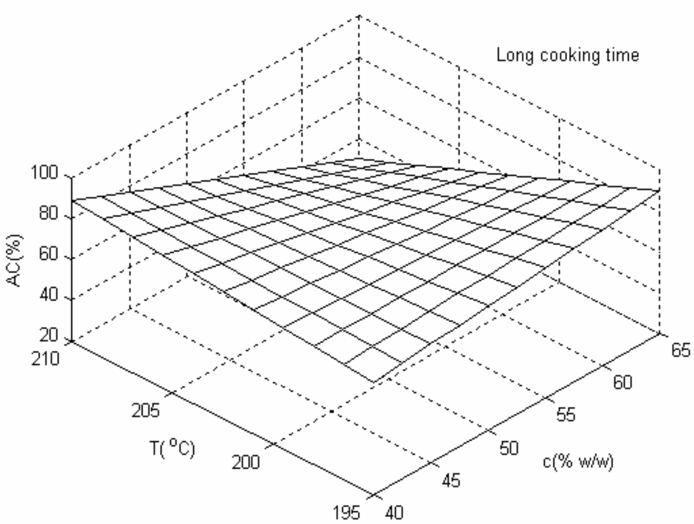

Figure 4: Variation of α-Cellulose vs. Ethanol Concentration and Cooking Temperature (180 min)

4 CONCLUSIONS

An experimental normalized design has been developed to describe the variation of pulp properties; i.e., pulping yield, kappa number, ash percent and α-cellulose in the soda aqueous ethanol medium at 10:1 liquor to raw material ratio. There was good agreement between the model and experimental data. As a result, the acceptable amount of α-cellulose was achieved at high cooking temperature and high ethanol concentration. At high ethanol concentration and low cooking temperature there was either poor delignification or high cooking yield and kappa number. At short cooking time (150 min), the lowest kappa number and α-cellulose were obtained at high ethanol concentration and high cooking temperature. However, in this case due to high ash content cooking yield was high. As a result, both high cooking temperature (210 °C) and ethanol concentration (65%w/w) and short cooking time (150 min) was recognized as optimum conditions to achieve the acceptable amount of α-cellulose content of the pulp.

NOMENCLATURE

AC= α-Cellulose in produced pulp (%)
AP= Ash Percent (100 × ash in pulp/ash in corresponding raw material; i.e., rice straw)
β_0 = constant of empirical correlations
β_i = linear coefficients of empirical correlations
β_{12} = non-linear coefficient of empirical correlations
C= ethanol concentration (% w/w)
KN= Kappa number of screened pulp
r^2 = Pearson's regression coefficient (Laplin, 1990)
t = cooking time, min
T= cooking temperature, °C
X_{max}= the highest value of independent variable in experimental data
X_{min}= the lowest value of independent variable in experimental data
x_i= Dimensionless, Normalized, independent variable ,e.g. $x_c=x_1$, $x_T=x_2$
y= dependent variable
Y= Total Cooking Yield (%)

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AUTHORS BIOGRAPHIES

SHAHRAM NAVAEE-ARDEH received his Master of Chemical Engineering from Tehran University in 2002. He joined Pulp and Paper Technology at AIT for pursuing his second master in 2003. He has published 4 International Journal papers and 7 National Conference Papers. He has been involved many research projects namely; Co-refining of mixed pulps (2004, UBC), Optimizing the bending stiffness of multi-layer paper and board (2003-04 AIT), Biodegradation of mixed hardwood bark into soil conditioner (composting process)(2002, The University of Tehran), organosolv pulping of rice straw and bagasse (2001, The University of Tehran), modification and thermopasticization of wood (1999, The University of Tehran). His research interests are fiber line technology, separation in chemical processes, simulation and modeling of chemical processes and biopulping and biobleaching technologies. His email address is < Shahram.navaee-ar@ait.ac.th>