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Acetosolv pulping modeling of oil palm frond fibers

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Abstract. Oil palm frond fibers were pulped using acetosolv pulping in laboratory scale batch digester. A central composite desigh was used to investigate the process and to study the effect of its variables on pulp quality and yield. A second order polynomial regression model, using three in dependent process variables, was found to be appropriate for describing acetosolv pulping oil palm fibers. The overall pulping conditions, which maximize yield while subject to a restriction of kappa number 19.93 were estimated at pulping time of 130 mins, a pulping temperature of 153 °C, AcOH of 85 % and HCl of 0.25 %.

Keywords: acetosolv pulping, oil palm frond fibres, yield, reponse surface methodology (RS).

Introduction

Oil palm, *Elaeis guineensis*, is an agricultural plant, which originates from west Africa and Cultivated in the tropical regions, particularly Malaysia and Indonesia for its oil producing fruit. Besides palm oil, the industry also generates massive amounts of lignocellulosic residues such as trunks and fronds during replanting and pruning, and the empty fruit bunches and the mesocarp fibres during miling. Depending on the type of residue, it is mulched, burnt as fuel, or burnt in the plantations, all of which offer limited values to the industries. Other utilizations are abovementioned residues, empty fruit bunches (EFB), with an estimated eight million tones of biomass being generated yaerly , has an added economical advantage of beiang already collected at the oil palm mills (Malaysia et al.2001)

Since the 1980's, several studies have been conducted on the suitability of this material as a source for pulp and paper . In earlier work , it is demonstrated that alkaline pulping of EFB using only sodium hydroxide appears to be the most interesting pulping process when its efficacy and environmental friendliness is taken into consideration (Akamatsu et al.. 1987; Khoo K.C & Lee T. W 1991; Wan Rosli W.D & Law L.N. 1988).

Pulping is however, a complex multivariable heterogeneous reaction process. In this system, the effect of single variable is not comparable unless all other conditions are fixed at the same condition, vis-a one –variable-at-a-time experiment. This approach is insufficient because it does not elucidate the effect of each individual factor, and the interactions between different factors cannot be followed [5]. One technique particularly suited to this application is Response Surface Methodology (RSM), which merges the methods of planned and efficient experimental desigh with least squares modeling to identify optimum conditions for the process response. The basic theoretical aspects, fundamental assumptions and the experimental implications of RSM have been discussed elsewhere (Myers, R.H & Montgometry, D.C 1995; Montgomery, D.C, 1997).

The objective of the present work is to develop a mathematical model in which the thee most important acetosolv pulping process variables, namely, pulping temperature, time at temperature and level are used to predict the response properties, viz.yield and kappa number. Basically, this process involves major variations namely perfoming the statistically designed experiments, estimating the coeffient in a mathematical model, and predicting the response and checking the adequacy of the Adequacy of the model.

Materials and Methods

Design of experiment

A central composite design (CCD) was used to outline the composition of the experimental process around a central combination. This type of design fulfils the requirement that all paramenters in the mathematical model can be estimated without an excessive number of number of observations, and that they be evenly spread over the whole experimental area of interest it consists of several components; for a thee independent variables process (k=3), this design consists of: (i) Factorial design points with eight (2^k, k =4) runs, (ii) Three centre points. The central combination for the experimental design was as follows: acetic acid,AcOH = 75%, HCl = 0,50% cooking temperatute,T = 140°C, and time-at-temperature, t = 120 mins.

Table 1 describes the detailed experimental design with actual and coded experimental values, with the later calculated by equations 1 to 4 below

$AcOH_{code}$ = (AcOH- 75%) / 20% (1)
HCl_{code} = (HCl –0.50%)/ 0.50% (2)
t_{code} = (t – 120 min)/ 60 min (3)
T_{code} = (T – 140°C)/ 30 °C (4)
All experiments were performed in duplicate.

Table 1. The actual (coded) experimental values used in the design of experiment

No Number	Pulping Variables				Response	
	AcOH %	HCl %	Time t	Temperature	Screened Yield %	Kappa Number
1	65	0.25	90	125	39.68	57.54
2	85	0.25	90	125	35.02	33.59
3	65	0.75	90	125	38.35	57.48
4	85	0.75	90	125	39.17	29.45
5	65	0.25	150	125	40.11	46.64
6	85	0.25	150	125	35.87	24.1
7	65	0.75	150	125	39.52	38.45
8	85	0.75	150	125	35.66	27.98
9	65	0.75	90	155	38.35	57.48
10	85	0.25	90	155	42.89	20.3
11	65	0.75	90	155	33.18	43.09
12	85	0.75	90	155	42.26	19.87
13	65	0.25	150	155	36.03	37.84
14	85	0.25	150	155	48.82	21.19
15	65	0.75	150	155	34.2	34.5
16	85	0.75	150	155	43.26	19.82
17	55	0.50	120	140	33.21	55.41
18	95	0.50	120	140	40.62	22.49
19	75	0	120	140	45.37	39.48
20	75	1	120	140	42.17	18.71
21	75	0.50	60	140	41.82	38.64
22	75	0.50	180	140	35.27	21.81
23	75	0.50	120	110	31.68	44.33
24	75	0.50	120	170	32.48	19.55
25	75	0.50	120	140	36.49	27.56
26	75	0.50	120	140	37.09	29.16
27	75	0.50	120	140	37.87	19.74
28	75	0.50	120	140	40.48	26.27
29	75	0.50	120	140	38.98	22.91
30	75	0.50	120	140	36.69	24.77

Raw Material

Oil palm frond samples were obtained from the palm oil mill PT Fajar Baizury, Aceh Indonesia. These fronds were cut at an approximate length of 2 inch and were dried before used.

Pulping

Pulping trials were carried out in a 4-litre stationary stainless steel digester manufactured by NAC Autoclave Co. Ltd., Japan filled with a computer-controlled thermocouple. The conditions employed throughout the experiment are as follows: liquor to material ratio of 10:1 and time to maximum temperature of 90 mins. At the completion of the cook, the pulps were. Mechanically disintegrated in a three-bladed mixer for 1 minute at a pulp consistency of 2.0% and subsequenfly screened on a flat-plate sreen with 0.15mm slits Sreened yield was determined gravimetrically after drying for 24 hours at 100^{o}C, whilst Kappa number by Tappi method T235.

Results and Discussion

Regression analysis

Table 1 summarises the results obtained from the caustic of OPF. Due to the multivariate nature of the present study, classical or single variable analysis is obviously inadequate. Hence response surface methodology was employed to analyse the pulping variable effects. For the 2k + 2K + 1 (k=3) experimental design used in this study, the variability of input variables is sufficient to allow a calculation of unfounded estimates of linear, quadratic and second-order interaction effects from the full factorial experiments. Thus, equation (4), a second-order polynomial, was employed to perform the analysis.

$$Y = a_o + \sum_{i}^{k} \beta X_i + \sum_{I}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j$$

Where, $X_i = \frac{X - X}{X_{max} - X_{min}}$

The response Y represents the dependent variable (response) of yield and Kappa number, whilst (X_is) are the independent variables comprising of acic asid, AcOH, HCl, cooking temperature and time at temperature. βs are the estimates of regression parameter computed by the least-squares method or named as named as least squares coenfficients. The X_i terms in the equation account for the linear effects of pulping variables, the X_iX_i terms for the quadratic effects and X_iX_i for the two-variable interaction effect. This model contains one contant, three quadratic terms, and three two-variable interaction effects. This model contains one contains one contant term, three quadratic terms, and thee two-variable interaction terms, a total of 10 parameter.

Multiple regression analyses were carried out with the first order terms and all possible combinations of second order and interaction terms, to find the fit for the response variables. The aim was to create a simple and pratical model with a minimum of equation terms,i.e. to prevent overfitting in the model. The decision to include second order and interaction terms was based on maximization of the R2 adjusted (percentage of variance accounted for by the regression, adjusted for the number of regression parameters) and the t-test for the individual regression coenfficients (rejection of the zero hypothesis of not effect if $|t| \geq 2$, with a type || error of 5%). The first order terms,X_i, were included in the model on the same criteria or when the corresponding interaction on second order term was selected in the model.

The estimated regression confficients and the significance values, Prob > |t| for each parameter of the best fit models are listed in Table 2. The coefficients a_o represent the estimated response values for the central combination of conditions. Both Kappa number and pulp yield were found to be satisfactorily fitted by all (nine) parameters with significant interactions between all the variables.

Table 2. Coefficients and statistics for the estimated regression equations

Variables	Kappa Number	Prob > t	Parameter	
			Screened Yield	Prob >t
a_o	25.07		37.93	
AcOH	-9.38	<0.0001	1.93	0.0002
HCl	-2.18	0.0229	-0.40	0.3327
t	-3.52	0.0009	-0.28	0.5034
T	-5.34	0.0001	0.62	0.1433
AcOH*AcOH	3.79	0.0003	-0.10	0.7931
HCl*HCl	1.33	0.1183	1.61	0.0006
t*t	1.61	0.0630	0.31	0.4264
T*T	2.04	0.0225	-1.31	0.0033
AcOH*HCl	0.41	0.7017	0.27	0.5887
AcOH*t	1.92	0.0882	-0.27	0.5887
AcOH*T	0.66	0.5379	3.46	<0.0001
HCl*t	-0.46	0.6685	-0.85	0.1062
HCl*T	0.40	0.7121	-0.46	0.3691
t*T	1.93	0.0867	0.54	0.2913
R^2(%)	93.52		88.74	

Note:

1) All the coefficients are in terms of the coded factors since the size of coefficients in a coded model directly to the observed change in the response and the coefficients in actual model cannot be compared to one another due to their dependence on unit of measure.

2) The significant value, Prob> |t|, is the probability of getting a larger value of |t| under a null hypothesis that parameter is truly equal zero. The smaller the Prob>|t| value, the more significant is the parameter.

Model fitting

Fitted values calculated from the estimated polynomial equations are compared with experimental results for kappa number and pulp yield in Figure 1. The model gives a good fit for the pulping data as indicated by R^2 value of 93.52% and 88.74% for kappa number and pulp yield respectively. The somewhat lower value for kappa is most likely due to the high sensitivity of its dependent variables to differences in pulping conditions which were probably not captured by the model and also due to the variations in the raw material.

Response Surface Analysis

Because of the complexities of equation (4), it is not an easy task to gain visual perception of the shape of the variability of a response variable in a specified input spance. Since the input spance itself is three dimensional, one independent variable has to be fixed when a three-dimension response surface is prepared. Therefore equation (4) may be used to generate different types of graphs based on one's particular interests; some of which are shown in Figures 2a,b and 3 a,b

Table 3. The experimental values and calculated values of responses of pulps prepared By selected optimum acetosolv pulping condition

Response	Mean (actual value)	Predicted Value	Difference, % (on actual value)
Kappa number	19.93	18.14	1.12
Screened yield	45.00	45.73	0.73

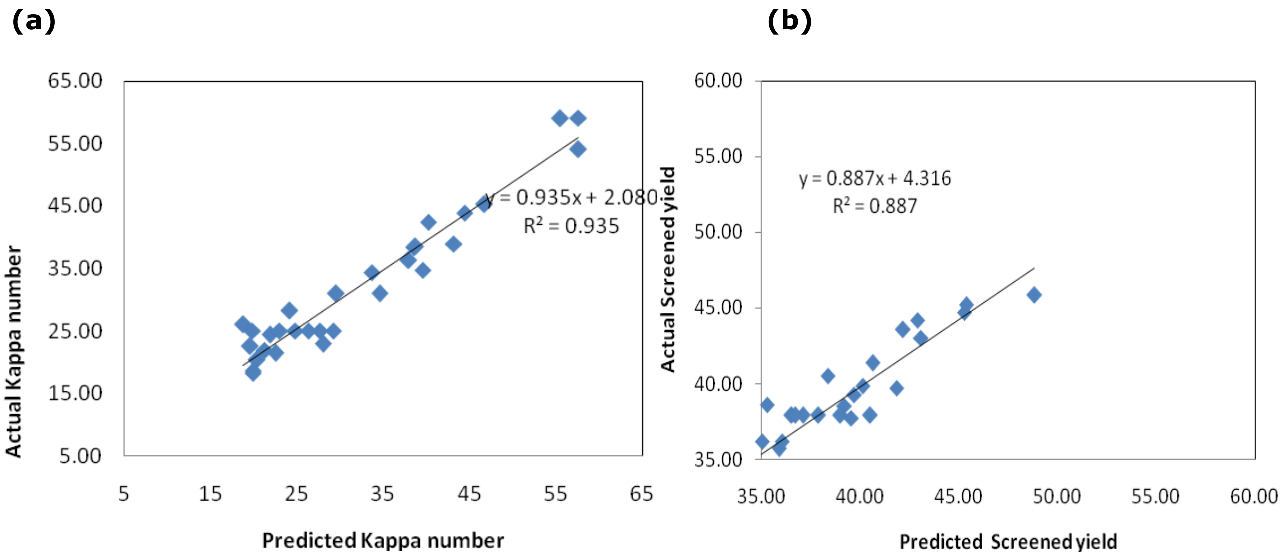

Figure 1. **(a)**. Actual Kappa number versus Predicted values for acetosolv pulping of oil Palm Fronds ; **(b)**. Actual screened yield versus Predicted values for acetosolv pulping of oil Palm Fronds

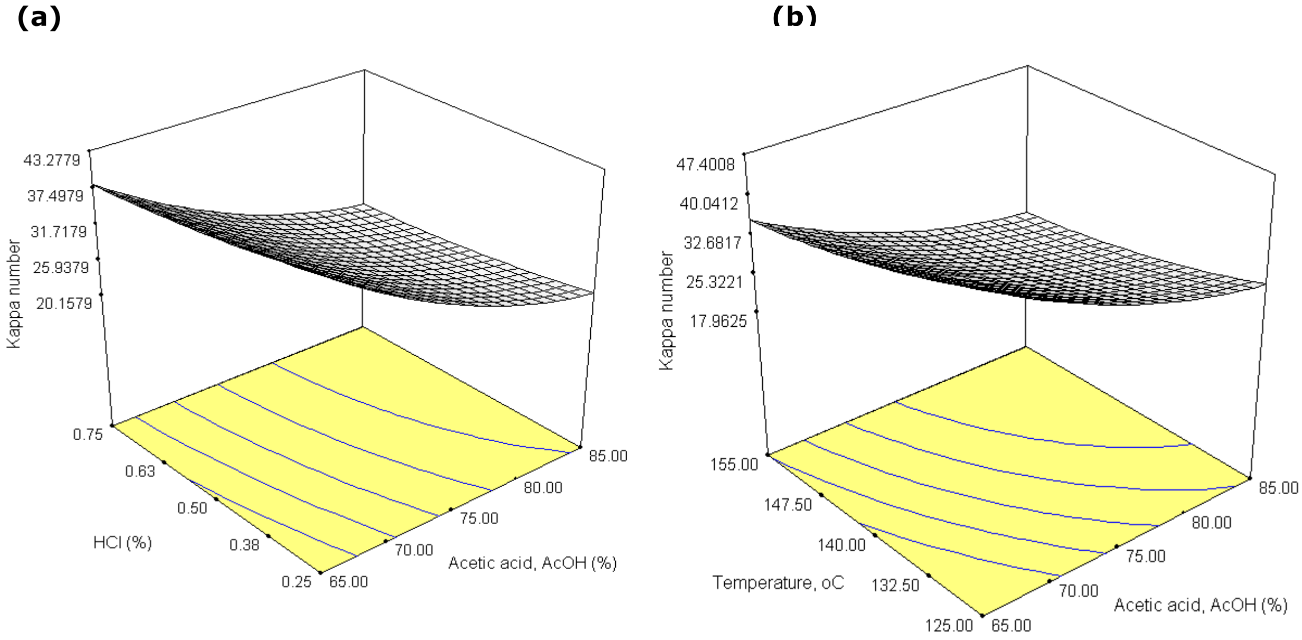

Figure 2. **(a)** Dependence of Kappa number on HCl and acetic acid at constant time of 120 mins and pulping temperature 140 °C; **(b).** Dependence of Kappa number on pulping temperature and acetic acid at constant HCl of 0,5% and time 120 mins

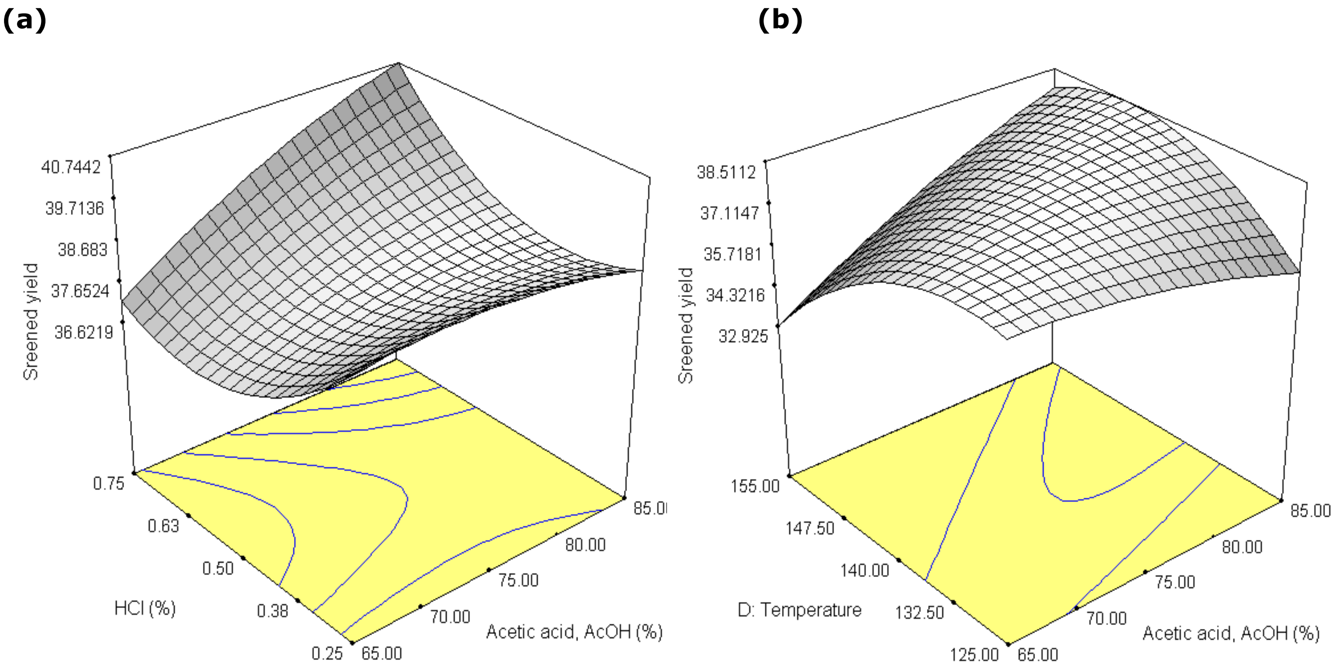

Figure 3. **(a)**. Dependence of Screened Yield on HCl and acetic acid at constant time of 120 mins and pulping temperature 140 °C; **(b)**. Dependence of Sreened yield temperature and acetic acid at constant time of 120 mins and HCl 0.50 %

Optimum conditions

Determination of the optimal process conditions for desired pulp quality requires a compromise with respect to all of response variables, viz. Kappa number and pulp yield. Optimization of an industrial-scale process is a more complex matter sice technical limitations and economic aspects should also be considered. Nevertheless, adequacy of the model equations for estimating optimum response values was tested with the conditions of maximum yield and Kappa number of 20. Table 3 shows the comparison of the calculated response values and the real experimental response values as a mean of two tests. The differences between the experimentally obtained and the calculated responses were, thus verifying the estimation models built though the statistical experimental design.

Conclusions

Second order polynomial regression models were found to be appropriate to describe the acetosolv pulping process Oil Palm Frond Fibres as a function of AcOH, HCl, time and temperature. The estimated models gave good predictions for Kappa number and Screened yield, as indicated by R^2 of 93.5 % and 88.7 % respectively. The optimum acetosolv pulping parameters, which maximizes pulp yield given the constraint of Kappa number 19.93 were estimated to be at a pulping temperature of 155 °C.. AcOH of 85 %, HCl of 0.25 % and a time at temperature of 130 min. The model equations for the response variables predicted values under these identified conditions were experimentally checked and proven to be adequately reproducible

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References

Malaysia Palm Oil Board (MPOB). 2001. Http/www.porim.gov.my.

Akamatsu, I., Kobayashi, Y., Kamishima, H., Hassan, K., Mohd Yusoff, M.N., Husin, M. and Hassan, A.H.1987. Industrial utilization of oil palm by-products II: Thermomechanical pulping of empty fruit bunches, *Cellulose Chemistry and Technology,* 21, 191-197

Khoo K.C. and Lee T.W (1991). Pulp and paper from the oil palm, Appita, 44(6), 385-388.

Wan Rosli W.D. and Law L.N. (1988). Chemical pulping of oil palm empty fruit bunches, *Cellulose Chemistry and Technology* 32, 133-143

Myers, R.H. and Montgometry, D.C 1999. Response surface methodology: Process and product optimization using designed experiments, New York: John Wiley & Sons. Inc.

Montgomery, D.C. (1997). Design and analysis of experiments, 4th edn. New York: John Wiley & Sons, Inc.

Parthasarathy, V.R., Klein, R., Sundaram, V.S.M., Jameel, H. and Gratz, J.S. 1990. Hydrogen peroxide reinforced oxygen delignification of southern pine kraff pulp and short sequence bleaching, Tappi, 73(7), 177-187

Ott, L. 1988. An Introduction to Statistical Methods and Data Analysis, 3 rd edition PWS-Kent, Boston.