RESEARCH PAPER

MODELING OF ACETOSOLV PULP YIELDS FROM PLANTAIN STALK

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ABSTRACT
Organosolv pulping processes have been developed as a substitute to the conventional process because of its little or no emission into the environment. Plantain stalk was subjected to aceto-solv pulping at atmospheric conditions under the influence of three operating parameters, namely, concentration of acetic acid, H_2SO_4– catalyst and time. The influence of the operational variables on the pulp yield was evaluated using a second - order factorial design. The results showed that the highest pulp yield was 64.14 % which was obtained at the lowest value of the operational variables. The greatest influence on the pulp yield was caused by the concentration of acetic acid while the H_2SO_4– catalyst had the least. The polynomial equation derived predicted the pulp yields with errors less than 6 %.

Keywords: *Acetosolv, pulp yield, operational variables, factorial design*

INTRODUCTION

The increasing demand for pulp and paper products and the relatively high cost of pulp woods coupled with the high rate of deforestation, calls for the utilization of non-wood raw materials such as agricultural by-products, industrial crops and naturally growing plants as alternative or complimentary raw material in the production of pulp and paper (Svenningsen *et al.*, 1999; Waranyou, 2010). These non - wood agricultural materials have shorter maturation time and lower lignin contents as compared to woods. Hence they consume low pulping chemicals and are relatively easy to be delignified.

It is equally important to develop chemical pulping processes that are environmentally friendly and most appropriate for the processing of non - wood raw materials (Mohieldin, 2014). The conventional alkaline pulping process such as kraft pulping is not suitable for processing non - wood fiber. Alkaline pulping is not environmentally friendly because of the

sulphur containing compounds it emits into the environment (Pinkerton, 2007). Apart from this, alkaline pulping of non woods produces large amounts of hemi-cellulose, which is difficult to control without inherent loss in the pulp quality (Rousu *et al*., 2002). On the other hand, the acidic sulphite pulping process is also not desirable and has long been discontinued because of environmental concerns and the poor quality of pulp emanating from it (Bajpai, 2010; Saadia and Ashfaq, 2010).

In recent times, the organosolv pulping process has been developed as a substitute to the conventional process because of its environmental friendliness (Johansson *et al*., 1987). This pulping process utilized organic solvents such as alcohol or organic acids as the pulping liquor in the delignification of plant fiber (Ligero *et al*., 2005; Ferrer *et al*., 2013; Wildschut *et al*., 2013; Snelders *et al*., 2014). High temperatures are usually employed in the use of organic alcohol such as methanol and ethanol, while organic acids such as acetic acid (acetosolv) can be utilized at relatively low temperature and atmospheric pressure (Jahan *et al*., 2007). The acid can easily be recovered by distillation and subsequently recycled. In addition, the cellulose, hemicellulose and lignin contents can be separated by degradation in the aqueous acetic acid (Muurinen, 2000; Waranyou 2010).

Plantain stalk is available in most major markets in Nigeria as an agricultural waste that can be employed as non wood raw material in the pulp and paper industry. Although, the pulp and paper potentiality of the stalk under the soda pulping process has been considered (Ogunsile *et al*., 2006), the acetosolv pulping process has not been employed or modeled. The present study was aimed at modeling the pulp yields of acetosolv pulping of plantain stalk under three operational parameters, using the second - order factorial design.

MATERIALS AND METHODS
Material preparation
The plantain stalk used for the study was obtained from the plantain market in Sabo Ilesha Osun state Nigeria. The stalk was cut into pieces, washed with water and then sun dried. The plantain stalk was ground and sieved into about 2- 4 mm. It was kept in a sealed polythene bag at room temperature.

Characterization of experimental materials
The composition of the plantain stalk sample was determined to be 40.8 % cellulose, 8.5 % lignin, 11.8 % ash and 2.3 % alcohol-benzene extractives as described in our previous work (Omotoso and Ogunsile, 2009).

The pulping process
Acetic acid cooking liquor was prepared from a standard concentrated solution of ethanoic acid by serial dilution with de-ionized water. About 2.5 g stalk fiber was place in a 250 ml flask with the appropriate amount of acetic acid (60-90 % by weight), as the pulping liquor and H_2SO_4 (0.5-1.5 % by weight), as the catalyst. The solvent / plantain stalk fiber ratio was 20:1 wt/wt. The flask was fitted to a condenser and the mixture was heated slowly to about 100 ^{o}C and refluxed for the next 60 to 180 minutes. At the end of the pulping time, the resulting pulp was thoroughly washed with tap water, drained and dried.

Pulp yields
The pulp yield was determined gravimetrically after drying at 102 ^{o}C to a constant weight in the oven as follows:
Pulp yield (%) = 100 * Oven dry weight of pulp (g) / 2.5 (g)

Experimental design
(The central composite factorial design)
The central composite factorial design was employed to evaluate and quantify the effect of the operational variables on the pulp yields. The effect of the variables were quantified more precisely by choosing part of the experimental results and grouping them to form a first order full factorial design, with variables at two levels (2^3). Using this design, some of the experimental data were fitted to a first order polyno-

mial regression equation as implemented in the "SPSS" statistical package. Individual and second order interaction influences over the response surface of the independent variables were evaluated (Aknazarova and Kafarov, 1982; Khuri and Cornell, 1987).

The mathematical model was:
$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_{12} X_1 X_2 + a_{13} X_1 X_3 + a_{23} X_2 X_3 + a_{11} X_1 X_1 + a_{22} X_2 X_2 + a_{33} X_3 X_3$$
(1)

The response variable Y represents the pulp yield. The independent variables, X_1, X_2 and X_3 correspond to concentration of acetic acid (60 to 90 % by weight), H_2SO_4 - catalyst concentration (0.5 to 1.5 % by weight) and time (60 to 180 minutes) respectively. The values of the independent variables were normalized from –1 to +1 by using the equation:

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

Where:

X_n is the normalized value of acetic acid, H_2SO_4 -catalyst and time.

X is the absolute experimental value of the variable.

$\bar{X}$ is the mean of all the experimental values for the variable in question

X_{mas} and X_{min} are the maximum and minimum values respectively of such a variable.

The central point of the design corresponds to the following reaction conditions:

Concentration of acetic acid = 75 %

H_2SO_4 – catalyst = 1.0 %

Time = 120 minutes,

All normalized independent variables for the central points of the design were designated zero.

RESULTS AND DISCUSSION
Variation in pulp yields
The result of the pulp yields and operational variables is shown in Table 1. It was observed that the pulp yield ranges from 45.79 % to 64.14 %. Values of the acetosolv pulp yields varied from plant to plant under differently or similarly related reaction conditions. The values of the pulp yield obtained in this study (45.79 % to 64.14 %) were higher than values of 28.3 % to 33.8 % reported in our previous study where soda liquor was used to pulp the same plant material (Ogunsile *et al*., 2006). This showed that acetic acid would be preferred to soda pulping liquor especially when high pulp yield is desired.

The pulp yields were similar to 52.6 % obtained from *Miscanthus sinensis* bark by the acetosolv process (Ligero *et al.* 2005), 46.3 % for depithed cardoon (Cynara cardunculus) stalks (Ligero *et al.* 2007), 46.56 % for empty fruit bunches from palm oil industry (Ferrer *et al.* 2013) and an average of about 50% for four species of pine (Witayakran *et al.* 2014). However, the use of phosphinic acid and alkaline pre-extraction of the fiber resulted in a higher range of yields from 43.3 % to 79.4% reported for birch wood chips (Kangas *et al*., 2015).

Table 1: Effects of process variables on pulp yields

CH₃COOH (weight %)	H₂SO₄ (weight %)	Time (min.)	Pulp yield (%)
90	1.5	180	47.04
90	1.5	60	49.25
90	0.5	180	45.79
90	0.5	60	57.94
60	1.5	180	53.2
60	1.5	60	56.01
60	0.5	180	57.51
60	0.5	60	64.14
75	1.0	60	53.01
75	1.0	120	52.31
75	1.0	180	48.73

As seen in Table 1, pulp yields are affected by the concentration of the pulping liquor and the duration of the pulping process. Generally, pulping carried out at high concentration of acetic acid is associated with relatively low pulp yields. Low pulp yields are also obtained at long periods of pulping (180 minutes) as compared to short durations (60 minutes). Although high concentration of pulping liquor increases the dissolution and removal of lignin content, it also initiates the degradation of the carbohydrate and cellulose materials, leading to a low pulp yield. The effect is more pronounced the longer the pulping time. Thus, a compromise must be reached between concentration of pulping liquor and pulping time such that optimum but tolerable pulp yields are obtained. Optimization of process variables is therefore highly necessary for maximum lignin removal and optimum pulp yields (Ogunsile and Uba, 2012; Brahim *et al.* 2017).

Optimum concentration of acetic acid as a pulping liquor varied from plant to plant and the reaction conditions employed. An acetic acid concentration of 93.25 % was reported for *Miscanthus sinensis* bark; $\geq$ 71.3 % for cardoon bark (*Cynara cardunculus*); 86.25 % for empty fruit bunches from the palm oil industry and 95 % for four pine species including *Pinus kesiya*, *Pinus merkusii*, *Pinus caribaea*, and *Pinus oocarpa* (Ligero *et al.*, 2005, 2007; Ferrer *et al.*, 2013; Witayakran *et al.*, 2014). These values, however, depend on the duration of pulping, temperature, plant materials and the objective of pulping. Generally high concentrations of pulping liquor are usually employed especially for producing bleachable pulps. This reduces the bleaching loads and chemical required in the bleaching plants.

Central composite design
The absolute and normalized values of independent variables with the pulp yields are presented in Table 2. Experiments 1-15 allowed the calculation of different parameters in the regression equations a_i and a_{ij}. These were subsequently subjected to a T - test to check their

Table 2: Absolute and normalized values of operational variables with the yields

Experiment	Ac (%)	Cc (%)	t (min)	X_1	X_2	X_3	PY (%)
1	90	1.5	180	1	1	1	47.04
2	90	1.5	60	1	1	-1	49.25
3	90	0.5	180	1	-1	1	45.79
4	90	0.5	60	1	-1	-1	57.94
5	60	1.5	180	-1	1	1	53.2
6	60	1.5	60	-1	1	-1	56.01
7	60	0.5	180	-1	-1	1	57.51
8	60	0.5	60	-1	-1	-1	64.14
9	90	1.0	120	1	0	0	49.12
10	60	1.0	120	-1	0	0	55.89
11	75	1.5	120	0	1	0	53.5
12	75	0.5	120	0	-1	0	57.27
13	75	1.0	180	0	0	1	48.73
14	75	1.0	60	0	0	-1	53.01
15	75	1.0	120	0	0	0	52.31

Ac, Cc and t are the absolute values of CH_3COOH, H_2SO_4 and time; PY = Pulp yields . X_1, X_2, and X_3 are the normalized values of CH_3COOH, H_2SO_4 and time.

significance at 95 % confidence level.

The coefficients of the model equation and the statistical parameters establishing its validity are summarized in Table 3.

Table 3: Significant and non-significant regression parameters

Factor	Yield
a_0	52.41
a_1	-3.76
a_2	-2.37
a_3	-2.81
a_{12}	(-0.625)
a_{13}	(-0.615)
a_{23}	1.72
a_{11}	(-0.071)
a_{22}	2.95
a_{33}	(-1.56)
R^2	0.98
R^2 adj.	0.944
F	27.3

The non-significant parameters at 0.05 levels are in parenthesis

The pulp yield was related to the independent variables through the equation:

$$\text{Yield} = 52.41 - 3.76\ X_1 - 2.37\ X_2 - 2.81\ X_3 + 2.95\ X_2 X_2 + 1.72\ X_2 X_3 \tag{3}$$

The values of R, R^2 and adjusted R^2 were 0.99, 0.98 and 0.944 respectively. The different factor values of a_0, a_1, a_2, … the fitting parameters by which the effects of each of the independent variables on the dependent variable (experimental results) can be determined and compared (Ligero, *et al.*, 2007; Ogunsile and German, 2010). All calculations were performed with a statistics module of SPSS.

Values calculated from the polynomial equation above were plotted with the experimental results for the different response variables as shown in Fig. 1. The results showed good correlation between the experimental values and those predicted by the models.

Equation 3 allows the estimation of the variation of the yield with changes in each independent variable over the range considered while the other two remain constant. Non-significant parameters were dropped to obtain simpler equations. The equation showed that each of the operation variables, namely CH_3COOH, H_2SO_4 - catalyst and time had significant influence at 95% confidence level on the pulp yield as apparent from the values of a_1, a_2 and a_3, and Figs 1, 2 and 3 respectively. Fig. 1 represents the behaviour of the pulp yield with respect to the variations in time and CH_3COOH at a high constant H_2SO_4 – catalyst. Figure 2 is the pulp yield behaviour according to variation in the two acids, while figure 3 describes the yield with variation in time and H_2SO_4 – catalyst. There were also significant interaction between H_2SO_4 -catalyst and time (a_{23}) on one hand, and the quadratic effect caused by the H_2SO_4 –
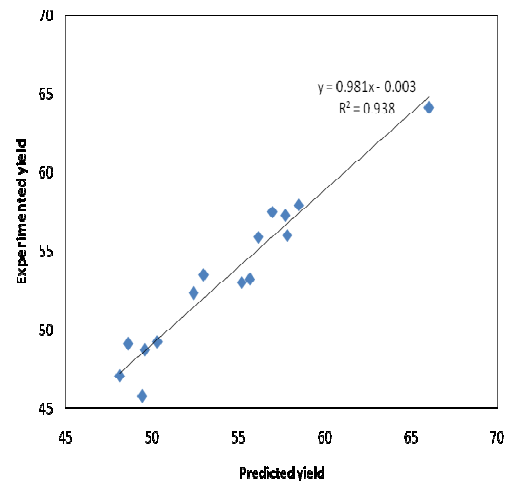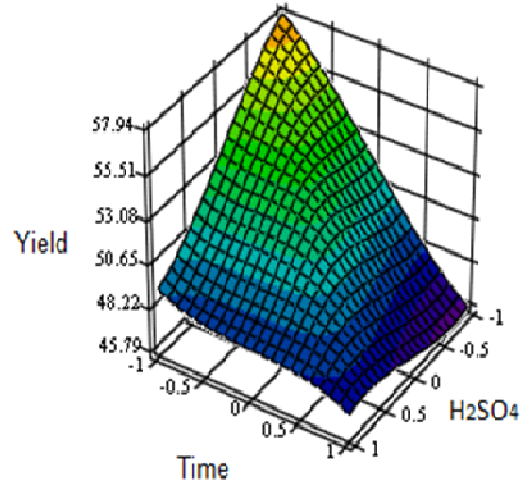

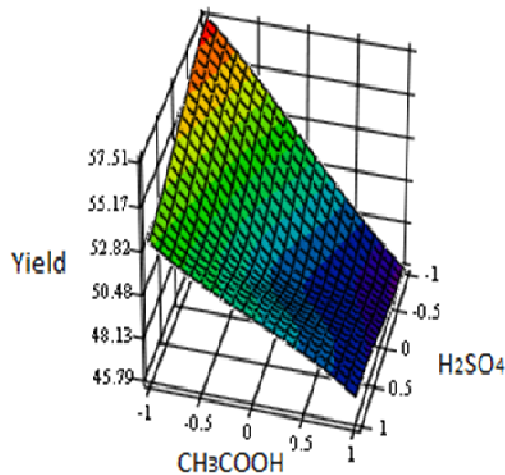**Fig. 1: Correlation between experimented and predicted values of pulp yield**
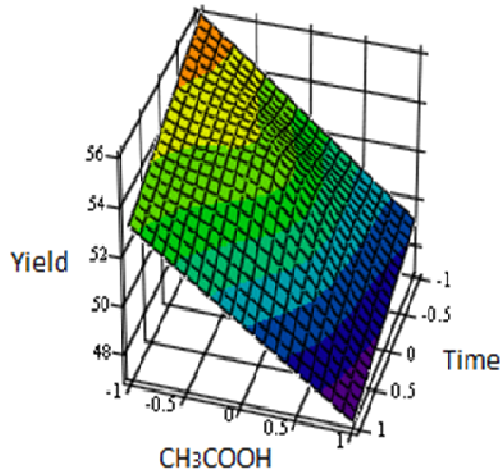
(Time, CH3COOH, Yield)

Fig. 2: Variation of the pulp yield with Time and CH₃COOH, at a constant concentration of H₂SO₄ - catalyst

(H2SO4, CH3COOH, Yield)

Fig. 3: Variation of the pulp yield with H₂SO₄ - catalyst and CH₃COOH at a constant Time

(H2SO4, Time, Yield)

Fig. 4: Variation of the pulp yield with H₂SO₄ - catalyst and Time at a constant concentration of CH₃COOH

catalyst (a_{22}).

According to equation 2, the lowest pulp yield (48.14 %) was obtained at large values of the three process variables (i.e. +1 for all). If yield similar to chemical pulp is desired, then all the process variables must be at normalized values of +1. However, this lowest yield can be raised to 55.66 % by using a low concentration of acetic acid (-1 normalized value), which will also bring a reduction in the amount of chemicals consumed. The highest predictable yield was 66.02 %, which occurs at low values of the process variables (-1 for all). A similar result was reported in the pulping olive tree trimming with ethanol where the highest pulp yield was obtained at low values of operational variables and vice versa. The maximum variation in the highest pulp yield was caused by changes in acetic acid concentration (a change of 7.52 units). This was reflected by the large negative slopes observed in Figs 1 and 2. The minimum variation in the highest pulp yield was caused

by changes in H_2SO_4 - catalyst concentrations (a change of 1.3 units) while the effect of time (2.18 units) lie in between as observed by the response graph of Fig. 3.

CONCLUSIONS
The study revealed the acetosolv pulping potentials of plantain stalk at atmospheric conditions. The pulp yields were successfully modeled using the second-order factorial design with errors less than 6 %. The optimum pulp yield was obtained at the lowest values of the operational variables, and was predicted to be 66.02 % compared to the experimented yield of 64.14 %. The maximum variation in the highest pulp yield was caused by changes in the concentration of acetic acid. This was followed by changes in time or duration of pulping, while changes in the concentration of H_2SO_4 – catalyst was the least.

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