Journal of the Korean Chemical Society
2012, *Vol. 56, No. 2*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2012.56.2.257

Optimization of Process Variables for the Soda Pulping of *Carpolobia Lutea* (Polygalaceae) G. Don

B. O. Ogunsile* and F. I. Uba
Department of Chemistry, University of Ibadan, Ibadan, Nigeria.
**E-mail: ogunsile@yahoo.com, bo.ogunsile@mail.ui.edu.ng*
(Received November 17, 2011; Accepted January 20, 2012)

ABSTRACTS. The selection of suitable delignification conditions and optimization of process variables is crucial to the successful operation of chemical pulping processes. Soda pulping of *Carpolobia* lutea was investigated, as an alternative raw material for pulp and paper production. The process was optimized under the influence of three operational variables, namely, temperature, time and concentration of cooking liquor. Equations derived using a second - order polynomial design predicted the pulp yield and lignin dissolution with errors less than 8% and 11% respectively. The maximum variations in the pulp yield using a second order factorial design was caused by changes in both time and alkali concentration. Optimum pulp yield of 43.87% was obtained at low values of the process variables. The selectivity of lignin dissolution was independent of the working conditions, allowing quantitative estimations to be established between the pulp yield and residual lignin content within the range studied.

Key words: *Carpolobia lutea*, Factorial design, Pulp yield, Residual lignin, Soda pulping

INTRODUCTION

Wood is a natural resource and a major raw material for the manufacture of pulp, paper and other similar products. Although wood is renewable, the rate at which wood is been used is not commensurate with the rate it is being replaced. The rate at which forests are declining has been estimated to be 13.0 million hectares per year in developing countries.[1]

In many developing countries of the world today, wood is becoming scarce and expensive because of the heavy dependence on wood for construction and building purposes, grazing, and conversion of forests to agricultural land to grow crops and felling of tree for firewood. The situation is further fueled and compounded by the increasing population, computer awareness, better literacy, improved communication, technology and industrialization.[2] The ecological damage cause by the continual use of wood includes deforestation, non-renewable energy consumption and greenhouse gas production.[3] The effects of deforestation are divers ranging from soil erosion, desertification, extinction of certain species, flooding, drought, climatic change and the disruptions of water and carbon cycle.[3,4]

The obvious solution to this is to use wood sparingly while embarking on the massive plantation and development of non-wood species. Non-woods fibers are abundantly available and have become one of the important alternative and supplementary sources of fibrous material[5,6] for pulp and paper making in some developing countries like China, India, Thailand and Indonesia.[2] In Nigeria there are vast amount of cellulose containing materials and agricultural residues majority of whose pulp and paper potentials have not been exploited.[7,8] *Carpolobia lutea* is a plant specie that belong to the family, polygalaceae. The plant requires good weather with hot climate and can survive adverse condition. It grows in small amount in dense form, sometimes seasonally like shrubs or as small trees up to 5 m high.[9] The stem of the plant is being used presently in Nigeria by the Hausa cattle rearers. Available literature showed that *Carpolobia lutea* has great medicinal properties,[10] but its pulp and paper potential has not been reported until recently.[11]

A number of ways can be used to study pulp quality as a function of process variables and optimize reaction conditions accordingly. In a complex heterogeneous reaction process like the soda pulping, a way of optimizing operating condition is the use of kinetic modeling based on mathematical design.[12] However; the mathematical model becomes too complex when more than two independent variables are involved. A better approach is the use of central composite factorial design.[13] Factor design is preferred to kinetic modeling because of its simplicity especially when severally variables are involved. The design had been applied to different vegetable materials where empirical model-

ing that uses several independent variables in order to identify patterns of variation in the dependent variables was developed.[14-20] In this study, soda process was employed to examine the delignification and pulping potentials of *Carpolobia lutea.* A second order factorial design was used to establish the operational conditions leading to optimum pulp yields and residual lignin contents.

EXPERIMENTAL SECTION

Raw Material

The plant *Carpolobia lutea* was collected at the Forestry Research Institute of Nigeria, Ibadan Nigeria. It was manually cut into chips of about 2-4 cm long and sun-dried. The proportions of the chemical constituents that affect the characteristics of the plant were determined on ground samples to be 44.06% cellulose (Kurschner-Hoffer), 25.96% lignin, 2.38% ash, 4.87% and 6.07% water and alcohol-benzene extractives respectively.[11]

Pulping Experiment

Soda cooking liquor was prepared from a standard concentrated solution of sodium hydroxide by serial dilution with de-ionized water. The samples were pulped in a 10-liter electrically heated stainless steel digester designed after the method of Grant.[21] Chips from the *Carpolobia lutea* were weighed and charged into the digester with the required amount of chemical solution at liquor to solid ratio of 7:1 and 10:1. The digester was heated to the operating temperatures (150 ºC and 170 ºC) and time (30, 90 and 150 minutes), which was then maintained throughout the experiment. The resulting pulps were thoroughly washed with tap water and the pulp yields were determined gravimetrically after drying at 102 ºC to constant weight in the oven. The pulps were analyzed for Kappa number as described in TAPPI standard.[22] The residual lignin was estimated from the Kappa number by multiplying with a factor of 0.13.[22]

The Central Composite Factorial Design

The effects of the operational variables on the pulp yields and residual lignin were evaluated and quantified using the central composite factorial design. Part of the data from the experimental result were chosen and grouped into a first order full factorial design, with variables at two levels (2^3). These data were fitted to a first order polynomial regression equation using the SPSS statistical package. Individual and second order interaction influences over the response surface of the independent variables were evaluated.

The mathematical model was:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2\ a_{13}X_1X_3 + a_{23}X_2X_3 \quad (1)$$

The response variable Y represents the pulp yield and residual lignin. The independent variables, and correspond to temperature, concentration of cooking liquor and time respectively. The ranges of values for each independent variable were:

Time: 30-150 minutes
Temperature: 150-170 ºC
Concentration: 8-12% NaOH solution.

The values of the independent variables were normalized from -1 to +1 by using the equation:

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

Where:

X_n is the normalized value of temperature, concentration and time

X is the absolute experimental value of the variable.

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

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

RESULTS AND DISCUSSION

Pulping Studies

Soda charge: The results and conditions of the pulping processes are presented in *Table* 1. There was a general decrease in the pulp yield and residual lignin due to an increase in the pulping liquor at a constant temperature and liquor to solid ratio. It was noticed that over half of the original material was dissolved after 30 minutes of pulping. This attested to the solving power of caustic soda as pulping liquor. The high dissolution of the initial material may also be attributed to the presence of highly soluble certain cell wall components such as fats, fatty acids, fatty alcohols, phenols, terpenes, resin acids and waxes. A detailed characterization of the waste liquor will reveal this. As observed from *Table* 1, increasing the alkali charge from 8% to 12% resulted in a decrease in the pulp yield from 43.18 to 31.85 after 30 minutes of pulping (experiments 1 and 7).The lignin content decreases slightly for the same period and markedly after 150 minutes of

***Table* 1.** Pulping conditions, pulp yields and residual lignin of *Carpolobia lutea*

Experiment No	Soda (%)	Liquor-to- solid ratio	Temperature (°C)	Time-at- temperature (minutes)	Pulp yield (%)	Residual lignin (%)
*1	8	7:1	150	30	43.18	4.46
2	8	7:1	150	90	37.11	3.51
*3	8	7:1	150	150	34.53	3.00
4	8	10:1	150	30	42.65	5.25
5	8	10:1	150	90	35.16	4.52
6	8	10:1	150	150	32.29	0.35
*7	12	7:1	150	30	31.85	4.34
8	12	7:1	150	90	30.27	2.76
*9	12	7:1	150	150	27.27	1.86
*10	8	7:1	170	30	34.53	2.77
11	8	7:1	170	90	28.72	1.33
*12	8	7:1	170	150	27.11	1.27
13	8	10:1	170	30	32.89	3.30
14	8	10:1	170	90	31.00	1.55
15	8	10:1	170	150	26.20	1.69
*16	12	7:1	170	30	30.16	1.63
17	12	7:1	170	90	23.10	1.33
*18	12	7:1	170	150	20.65	1.24

*data reported earlier.[11]

cooking (experiment 9). The effect of the alkali charge can be reduced by mixing it with certain percentage of organic solvent such as methanol and ethanol.[11,23] The presence of this solvent reduces the degradation effect of alkali while enhancing the dissolution of lignin.

Pulping time: Generally, the longer the period of pulping, the higher the degree of lignin removal and the lower the pulp yield. At a particular charge of effective alkali, pulping for 150 minutes at 170 °C resulted in the lowest yield while the highest yield was recorded for the pulp made for 30 minutes at 150 °C.

Pulping Temperature

There was a resultant decrease in the pulp yield and residual lignin as the temperature was increased from 150 °C to 170 °C. Lignin and cellulose are dissolved out at different rates during cooking and these rates are much accelerated by increasing the temperature.

Liquor to solid ratio (LS): Liquor to solid ratio had little effect on the pulp yield. In fact the pulp yield only decreased slightly from 43.18 to 42.65% (experiments 1 and 4), 37.1 to 35.16 (experiments 2 and 5) and 34.53 to 32.29% (experiments 3 and 6) respectively as the liquor to solid ratio was increased. This was expected so because there was no change in concentration of the cooking liquor. Only the volume was increased. However, a different result was obtained for the residual lignin which increases instead of decreasing. Apparently, as the pulping volume was increased, some of the dissolved lignin got re-absorbed onto the pulp matrix thereby increasing their lignin content.[24,25] According to Yu *et al*.,[25] the origin of such enrichment is complicated but occurs towards the end of the pulping and is influenced by certain factors such as the nature of fiber materials, conditions and methods of pulping, and the topochemistry of lignin dissolution. The phenomenon may be controlled by washing the resulting pulp first with a suitable organic solvent and finally with water. Alternatively the pulp may be bleached to keep the level of residual lignin permanently low.

The Factorial Design

The experimental design (2^3 factorial designs) together with the pulp yield and the residual lignin are presented in *Table* 2. Experiments 1-15 of *Table* 2 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 significance at 90 to 95% confidence level using the experimental error estimated from the central point of the design, that is, experiment 9 of *Table* 2. The central point of the design corresponds to the following reaction conditions:

***Table* 2.** Experimental design and result for yield and residual lignin

Experiment	X_1 Temperature	X_2 Concentration	X_3 Time	Yield (%)	Lignin (%)
1	1	1	1	19.05	1.24
2	-1	1	1	27.27	1.86
3	1	1	-1	30.16	1.63
4	-1	1	-1	31.85	4.34
5	1	-1	1	27.11	1.27
6	-1	-1	1	34.53	3.00
7	1	-1	-1	34.53	2.83
8	-1	-1	-1	43.18	4.46
9	0	0	0	33.65	1.60
10	1	0	0	26.90	1.29
11	-1	0	0	38.13	3.28
12	0	0	-1	34.61	2.21
13	0	0	1	25.72	1.17
14	0	1	0	26.06	1.55
15	0	-1	0	35.80	2.67

***Table* 3.** Signicative regression parameters

	Yield	Residual Lignin
a_0	32.0	1.709
a_1	-3.72	-0.868
a_2	-4.076	-0.361
a_3	-4.065	-0.693
a_{12}	(0.77)	(0.004)
a_{13}	(-0.663)	(0.249)
a_{23}	(0.048)	(0.019)
a_{11}	(0.932)	0.549
a_{22}	(0.653)	(0.374)
a_{33}	(1.418)	(-0.046)
R^2	0.971	0.993
R^2 adj.	0.899	0.952
F	13.40	28.85
Sig. F (%)	>98.8	>99.7

The non-significant parameters at 0.1 levels are in parenthesis

Temperature = 160 °C
Concentration = 10% soda
Time = 90 minutes

All normalized independent variables for the central points of the design are zero. The coefficients of the model equations and the statistical parameters establishing their validity are summarized in *Table* 3. The dependent variables (pulp yield and residual lignin) were related to the independent variables through the following equations:

$$\text{Yield} = 32.0 - 3.72X_1 - 4.08X_2 - 4.08X_3 \quad (3)$$

$$\text{Residual lignin} = 1.71 - 0.87X_1 - 0.36X_2 - 0.69X_3 + 0.55X_1X_1 \quad (4)$$

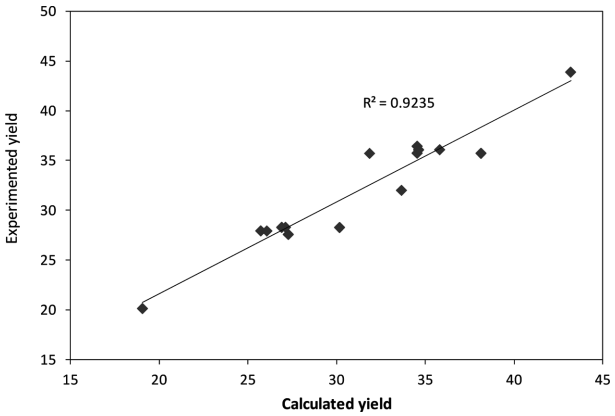

***Fig*. 1.** Correlation of Experimental and calculated yield.

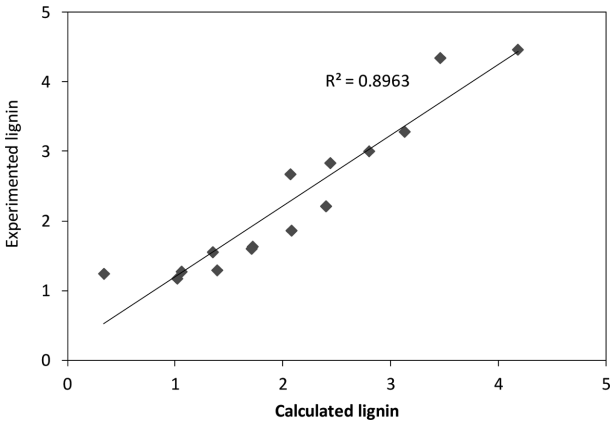

***Fig*. 2.** Correlation of experimented and calculated lignin.

Values obtained from equations 3 and 4 above were plotted with the experimental results for the different response variables. The plots as shown in *Fig*. 1 and *Fig*. 2 showed good correlation between the experimental values and those predicted by the models with errors less than 8% and 11% for the pulp yield and the residual lignin respectively. Estimation of the variation of the pulp yield with changes in each independent variable over the range considered was made from equation 3. In order to simplify the equations, non-significant parameters were dropped. It was observed from equation 3 that there was no significant interaction between any of the process variables and that the yield decreases as each of the process variable increases. The lowest pulp yield (20.13%) was obtained at large values of the three process variables (i.e. +1 for all). This implied that a low pulp yield similar to chemical pulp would be obtained when high values of temperature, time and concentration of cooking liquor are used. However, this lowest yield can be raised to 27.57% by pulping at a lower temperature and 28.3% using either low value of the concentration of cooking liquor or time

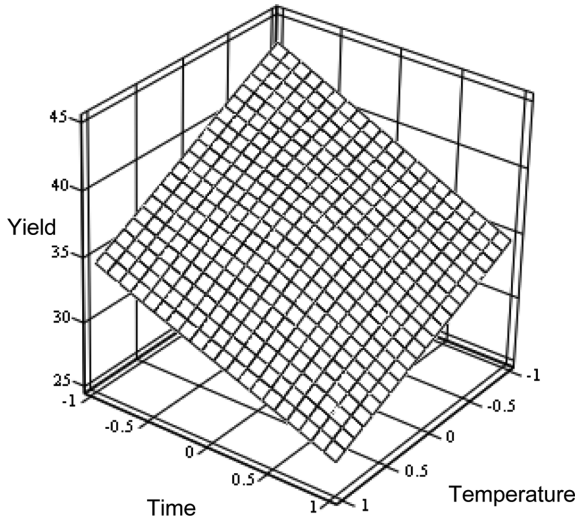

***Fig*. 3.** Variation of yield with time and temperature at a low constant concentration.

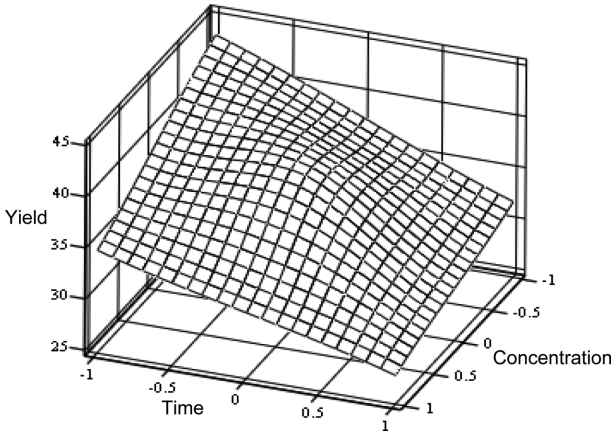

***Fig*. 4.** Variation of yield with time and concentration at a low constant temperature.

(-1 normalized value). The use of a low concentration of cooking liquor would result in some savings in the chemical consumed in addition to increasing the pulp yield. According to equation 3, the highest obtainable yield was 43.87%, which occurs at low values of the process variables (-1 for all). The minimum variation in the highest pulp yield was caused by changes in temperature (a change of 7.44 units) while the maximum variation was caused by changes in both time (a change of 8.16 units) and alkali concentration (a change of 8.14 units) respectively as observed in a_2 and a_3 of *Table* 3 and shown in *Figs*. 3 and 4. *Figs.* 3 and 4 revealed the variation of the pulp yield with time and temperature, and with time and concentration respectively.

The minimum lignin content of the soda pulp according to equation 4 was obtained at high values of cooking time,

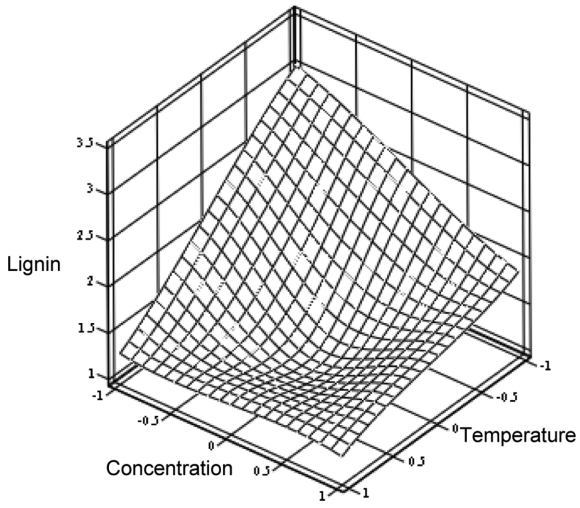

***Fig*. 5.** Variation of lignin with concentration and temperature at a constant high time.

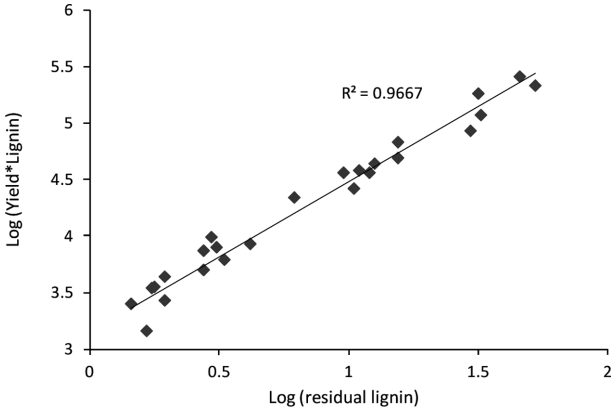

***Fig*. 6.** Selectivity graph of Soda pulping of Carpolobia lutea.

temperature and concentration. Under this condition, the highest and lowest variations in the minimum residual lignin content was caused by changes in temperature (1.74 units) and concentration of cooking liquor respectively (*Fig*. 5). Temperature had considerable influence on the residual lignin as illustrated by the large curves on the surface plot of *Fig*. 5. Changes in time (1.38 units) lie in between. Pulping at high temperatures for a short cooking time with low to medium concentration of pulping liquor would give the best compromise for both pulp yield and residual lignin content.

Selectivity of Lignin Dissolution

The selectivity graph (*Fig*. 6) was expressed as the logarithmic of the product of the yield and residual lignin.[26] The relatively high correlation between variables (r^2=0.97) indicated that quantitative estimations can be established between the yield and residual lignin content within the

***Table* 4.** Combined effects of time and temperature on the pulp yield and the residual lignin

Concentration of liquors	Liquors to solid ratio	Cooking temperature (°C)	Time (minutes)	Pulp yield (%)	Residual lignin (%)
8	7:1	150	150	34.53	3.00
8	7:1	170	30	34.53	2.83
8	10:1	150	150	32.29	2.96
8	10:1	170	30	32.89	3.30
12	7:1	150	150	27.27	1.86
12	7:1	170	30	30.16	1.63

***Table* 5.** Ratio of dissolved lignin to weight losses

Concentration of liquors	Liquors to solid ratio	Temp. (°C)	Time (min.)		
			30	90	150
8	7:01	150	0.38	0.36	0.35
8	7:01	170	0.35	0.35	0.34
8	10:01	150	0.36	0.33	0.34
8	10:01	170	0.34	0.35	0.33
12	7:01	150	0.32	0.33	0.33
12	7:01	170	0.35	0.32	0.31
	Average		0.35	0.34	0.33

range studied. It also showed that the selectivity of lignin solubility was independent of the working condition.

Combined Effect of Temperature and Time

The combined effect of temperature and time was evaluated by comparing some pairs of results as presented in *Table* 4. One of each pair represents pulping process carried out at low temperature (150 °C) for a long time (150 minutes) and the other at high temperature (170 °C) for a short time (30 minutes). The results showed that some of the pairs were relatively close. This implied that prolong cooking at low temperature may not necessary result in any increase in the total yield over that obtained for a short time at high temperature for the same degree of pulping. Pulping at high temperature for a short time may be more advantageous especially when high rate of delignification and substantial savings in time is required.

Ratio of Dissolved Lignin to Weight Losses

The ratio of the dissolved lignin to the weight losses ranged from 0.31 to 0.38 with an average of 0.34. The ratio decreases with increasing pulping time as presented in *Table* 5. This ratio can be used to estimate the quantity of lignin present in the pulp provided the pulp yield is known. The relatively close values seem to suggest that solubilization and delignification take place almost at the same rate.

CONCLUSIONS

A second - order polynomial design used for the optimization of soda pulping of *Carpolobia* lutea under the influence of temperature, time and concentration of cooking liquor predicted the pulp yield and lignin dissolution with errors less than 8% and 11% respectively. The minimum variation in the highest pulp yield was caused by changes in temperature while the maximum variation was caused by changes in both time and alkali concentration. The highest pulp yield was obtained at low values of the process variables. Temperature had considerable effect on the residual lignin content more than time and concentration of the cooking liquor. The selectivity of lignin dissolution was independent of the working condition but allows quantitative estimations to be established between the yield and residual lignin content within the range studied. The combined effects of temperature and time revealed that pulping at high temperature for a short time may be more advantageous especially when high rate of delignification and substantial savings in time is required. The ratios of the dissolved lignin to the weight losses were relatively close suggesting that solubilization and delignification take place almost at the same rate.

Acknowledgements. The authors wish to acknowledge the Senate Research Grants from the University of Ibadan, Nigeria. The technical assistance rendered in the design and construction of the pulp wood digester by Dr. Fadare, D.A. of the Department of Mechanical Engineering, University of Ibadan, Nigeria, is highly appreciated.

REFERENCES

1. Global Forest Resources Assessment, *FAO - Food and Agriculture Organization of the United Nations Rome*, 2005.
2. Ashori, A. *Polymer-Plastic Technol. Eng.* **2006**, *45*, 1133.
3. Kissinger, M.; Fix, J.; Rees, W. E. *Ecological Economics*, **2007**, *62*, 552.
4. West, T. O.; Marland, G. *Agriculture, Ecosystems & Environ.* **2002**, *91*, 218.
5. Chauhan, L.; Dhawan, S.; Gupta, S. *Journal of the T.D.A.* **2000**, *46*, 11.
6. Jiménez, L.; Rodrígueza, A.; Péreza, A.; Morala, A.; Serranoa, L. *Ind. Crops Prod.* **2008**, *28*, 11.
7. Raw Material Research and Development Council (RMRDC). *Report on the Techno-Economic survey of the multi-disciplinary task force on pulp, paper products printing and publishing sector*, Lagos, Nigeria, 1996.
8. Oluwadare, A. O. *J. Trop. For. Resour.* **1998**, *14*, 110.
9. Inyang, E. *The Verdict Press* **2003**, *1*, 111.

10. Ettebong E.; Nwafor, P. *African J. Biotech.* **2009**, *8,* 12.
11. Ogunsile, B. O.; German C. Q. *Biores.* **2010**, *5*(4), 2417.
12. Tjeerdsma, B. F.; Zomers, F. H. A.; Wilkizon, E. C.; Sierra-Alvarez, R. *Holzforschung* **1994**, *48*(5), 415.
13. Aknazarova, S.; Kafarov, V. *Experiment Optimization in Chemistry and Chemical Engineering*; Mir Publishers: Moscow, 1982.
14. Vazquez, G.; Antorrena, G.; Gonzalex, J. *Holzforschung*, **1995**, *49*, 69.
15. Vega, A.; Bao, M.; Lamas, *J. Biores. Technol*. **1997**, *61*, 1.
16. Gilarranz, M. A.; Oliet, M.; Rodriguez, F.; Tijero, J. *Canadian J. Chemical Engineering* **1999**, *77*(3), 515.
17. Lopez, F.; Dýaz, M. J.; Eugenio, M. E.; Ariza, J.; Rodrýguez, A.; Jimenez, L. *Biores*. *Technol*. **2003**, *87*, 255.
18. Ligero, P.; Vega, A.; Ba, O. M. *Ind. Crops Prod*. **2005**, *21*, 235.
19. Jiménez, L.; Angulo, V.; Caparros, S.; Ariza, J. *Biores. Technol*. **2007**, *98*, 3440.
20. Dutt, D.; Upadhyay, J. S.; Singh, B.; Tyagi, C. H. *Ind. Crops Prod.* **2009**, *29*, 16.
21. Grant, J. *A Laboratory Handbook of Pulp and Paper Manufacture*, 2nd ed.; Edward Arnold Ltd: 1961; p 49.
22. TAPPI. *Kappa number of pulp T236CM-85*. 1993.
23. Lopez, F.; Garcia, J. C.; Perez, A.; Garcia, M. M.; Feria, M. J.; Tapias, R. *Chem. Engr. Res. Design: Transaction of the Institution of Chemical Engineers Part A* **2010**, *88*(1), 1.
24. Laine, J.; Stenius, P. *Cellulose* **1994**, *1*, 145.
25. Yu, Y.; Koljonen, K.; Paulapuro, H. *Ind. Crops Prod*. **2002**, *15*, 123.
26. Masura, V. *TAPPI J.* **1993**, *76*, 105.