MODELING OF SODA - ETHANOL PULPS FROM *CARPOLOBIA LUTEA*

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The chemical properties and soda-ethanol pulping of *Carpolobia lutea* was investigated as an alternative raw material for pulp and paper production. The influence of temperature, time, and concentration of pulping liquor on the pulp yields and residual lignin contents was evaluated using a central composite design. The maximum variation in the minimum residual lignin content was caused by changes in time, while temperature and time were responsible for the variation in the highest pulp yield. A maximum pulp yield of 48.53% was obtained at low values of the process variables. The selectivity of lignin dissolution was independent of the working conditions but allowed quantitative estimations to be established between the yield and residual lignin content within the range studied. 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.

Keywords: Carpolobia lutea; Factorial design; Pulp yield; Residual lignin; Soda-ethanol pulping

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INTRODUCTION

In the history of pulp and paper making, the initial raw materials were obtained mainly from old clothes or worn out linen from flax cotton fiber and hemp (Van Roekel 1994). The fibers from these materials were soaked in water, beaten, intermixed, and then lifted up from the water with the aid of a sieve to obtain the paper. As the demand for paper increased, rags became scarce and were not readily available. Wood therefore became the dominant source of fibers for the pulp and paper industry.

However, the increased cost of pulp wood and its scarcity in many countries of the world have directed attention to the use of non-woods and certain agricultural residues. Non-wood fibers are abundantly available and have become one of the important alternative and supplementary sources of fibrous material for pulp and paper making in some developing countries including China, India, Thailand, and Indonesia (Ashori 2006). Other non-woods that had been considered include abaca (Jiménez et al. 2005), *leucaena* varieties (Díaz et al. 2007), rice straw (Rodríguez et al. 2008a), various agricultural residues (Jiménez et al. 2008; Yaghoubi et al. 2008), empty fruit bunches (Rodríguez et al. 2008b), *hibiscus* species (Dutt et al. 2009), canola stalks (Enayati et al. 2009), rice stem fibers (Alireza and Pejman 2010) and palm fruit fibers (Sridach 2010). The utilization of non-woods as raw materials in the making of paper offers some

benefits, which include easy delignification because of their low lignin contents, short maturation time of about a year or two, and low energy requirements. Furthermore, non-woods can be used to produce different grades of papers ranging from newsprint, writing, printing, liner board, tissue, currency, security, filter, tea bags, and high grade books (Rangamannar 1997).

Among the conventional pulping processes, soda pulping is less polluting and more environmentally friendly. During soda pulping, there is appreciable degradation of cellulose fibers. Addition of a suitable organic solvent such as ethanol reduces the dissolving power of the liquor and protects the cellulose fiber from its degradating effect, thereby enhancing the pulp yield (Hergert 1998; Idarraga 1999; Sahin 2003; López et al. 2006, 2010). In the soda-ethanol pulping of jute, Sahin (2003) reported that delignification proceeded more rapidly and more selectively, resulting in a marked improvement of the strength properties of the pulp.

Optimization of process variables is highly essential in a complex heterogeneous reaction process such as chemical pulping. This process is geared towards achieving production and quality while minimizing time, effluents, and consumption of chemicals and energy (Jansson 2004; López et al. 2006). One of the proactive ways of doing this is through the use of kinetic modeling based on mathematical design (Tjeerdsma et al. 1994). However, the complexity of the mathematical modeling, especially when more than two variables are involved, renders this method limited. Another approach is the use of the central composite design (Aknazarova and Kafarov 1982; Montgomery 2001). Unlike the kinetic model, the factor design do not becomes complex when several variables are involved but allows the development of empirical models for the various independent variables in order to identify patterns of variation in the dependent variables of various pulping processes (Vazquez et al. 1995; Vega et al. 1997; Gilarranz et al. 1999; López et al. 2003; Jiménez et al. 2005; Rodríguez et al. 2008a; Yaghoubi et al. 2008; Hedjazi, et al. 2009 López et al. 2010). *Carpolobia lutea* is a plant species belonging to the family *polygalaceae*, whose pulp and paper potential has not been reported. The present study reports the chemical properties of the plant and the variable optimization of the pulp yield and residual lignin content under the soda ethanol pulping process.

EXPERIMENTAL

Material

Carpolobia lutea requires good weather with hot climate and can survive under adverse conditions. It grows seasonally like shrubs or as small trees up to 5 m high (Inyang 2003). The stem of the plant is being used presently in Nigeria by the Hausa cattle rearers. Available literature shows that *Carpolobia lutea* has great medicinal properties (Ettebong and Nwafor 2009). *Carpolobia lutea* was collected at the Forest Research Institute of Nigeria, Ibadan Nigeria. The plant was manually cut into chips of about 2 to 4 cm long, sun-dried, and stored at room temperature in a polythene bags until it was ready for analyses.

Chemical Analysis

The proportions of the chemical constituents that affect the characteristics of the plant were determined on ground samples of *Carpolobia lutea*. The following ASTM standard methods were used for the water soluble components – ASTM D1110-56 (1968), alcohol-benzene extractives – ASTM D1107-56 (1972), one percent caustic soda solubility – ASTM - D1109-56 (1972), and ash contents – ASTM D1102-56 (1972) of the samples. The Kurschner-Hoffer cellulose method (1931) was used for the cellulose, while the standard method of TAPPI was used for the lignin (1998).

Pulping Experiments

The caustic soda cooking liquor was prepared from a standard concentrated solution of sodium hydroxide. Soda-ethanol liquor was prepared by mixing an equal volume of the soda liquor with ethanol/water (60/40, v/v) solution. The samples were pulped in a 10-liter electrically heated stainless steel digester, which was designed using the method of Grant (1961). Chips from the *Carpolobia lutea* were weighed and charged into the digester with the required amount of chemical solution at a liquor-to-solid ratio of 7:1 and 10:1. The digester was heated to the operating temperatures (150°C to 170°C) and time (30 to 150 minutes), which was then maintained throughout the experiment. The resulting pulp was thoroughly washed with tap water, and the pulp yield was determined gravimetrically after drying at 102°C to constant weight in the oven. The pulps were analyzed for Kappa number, and the residual lignin was estimated from the Kappa number by multiplying with a factor of 0.13 as described in the TAPPI standard (1993).

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 and residual lignin. 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. Using this design, some of the experimental data were fitted to a first order polynomial regression equation using the Statgraphic 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 X_1, X_2 and X_3 correspond to temperature, concentration of cooking liquor, and time respectively, and $a_{0,j}$, …, $a_{2,3}$ are the regression coefficients. The ranges of values for each independent variable were: time, 30-150 minutes, temperature 150-170°C, and concentration 8-12 % NaOH solution. The ratio 60/40 (v/v) of the ethanol/water mixture was used because it gave the highest pulp yield and minimum lignin contents in a trial run.

The values of the independent variables were normalized from –1 to +1 by using the equation,

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

where: X_n is the normalized value of LS, time, temperature and concentration, 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

Chemical Composition

The result of the chemical analysis and identification are presented in Table I. The values of the extractives, i.e., hot water solubility (4.87%) and alcohol-benzene extractives (6.07%) were moderate and comparable to values of 3.24 to 7.8% and 6.10 to 10.36 %, respectively reported for most non-woods (Jiménez et al. 1990; Díaz et al. 2007; Gonzalez et al. 2008). The one percent caustic soda solubility was high but not as high as 57.7% reported by Rodríguez et al. (2008c). The caustic soda solubility of *Carpolobia lutea* revealed the level of fungal attack in the plant. The high value may also be due to the easy penetration and degradation of the cell wall by the alkali (Kristova et al. 1998). The content of mineral salts in the *Carpolobia lutea* as indicated by the ash content was favourably low. Values as high as 7.9 and 11.0% were reported for sunflower stalk (Kristova et al. 1998; López et al. 2005). High ash content is undesirable for pulping processes because it increases the normal consumption of chemicals and complicates the recovery of waste liquors. The lignin content was in the upper range of 10.8 to 26.3% reported for most non-woods (Rodríguez et al. 2008). This may lead to high chemical consumption or a long pulping cycle. The cellulose content of 44.06% was an indication of an average but tolerable pulp yield.

Table 1. Chemical Composition of *Carpolobia lutea* (% oven dry raw material)

Component	Amount (%)
Ash	2.38
Extractives:	
Hot water	4.87
Alcohol-benzene (1:2)	6.07
1 % NaOH	21.01
Lignin	25.96
Cellulose, Kurschner-Hoffer	44.06

Pulping Studies

Concentration of cooking liquors

The results and conditions of the pulping processes are presented in Table 2. Generally, increasing the concentration of sodium hydroxide in the cooking liquor increased the rate of lignin dissolution but resulted in about 4 to 12% decrease in the pulp yields. Addition of ethanol to the soda cooking liquor resulted in an increase in the pulp yield even at high concentration and temperature. For example, the pulp yield was increase from 43.18 to 48.53 % (experiments 1 and 3) and 34.53 to 40.02 % (experiments 7 and 9) after 30 minutes of pulping at 150^{o}C and 170^{o}C respectively. This result was in line with the findings of Sahin (2003) in the soda-ethanol pulping of jute. However, the assertion that ethanol addition promotes delignification was not observed here. Instead, there was an increase in the residual lignin content. The reason for this was not immediately clear but may be attributed to the pulping method employed. In the present situation, a stationary digester was used, which allowed most of the ethanol used to be evaporated toward the end of each cooking scheme. The dissolved lignin was therefore precipitated and reabsorbed into the pulp matrix as the solvent evaporated, thereby increasing its lignin content. This agreed with the conclusion of Xu et al. (2007) that high kappa number or residual lignin of ethanol pulp was mainly due to the precipitation of the dissolved lignin from the pulping liquor.

Pulping time and temperature

There was an increase in delignification and a decrease in the pulp yield as the period of pulping and temperature increased. Lignin and cellulose were dissolved out at different rates during cooking, and these rates were much accelerated by increasing the temperature. At a particular charge of effective alkali, pulping for 150 minutes at 170^{o}C resulted in the lowest yield, while the highest yield was recorded for the pulp made for 30 minutes at 150^{o}C. In all, more than half of the original material was dissolved after 30 minutes of pulping. The high dissolution of the initial material may be attributed to the dissolving power of the caustic soda, fungal attack, and the easy penetration of the cell wall, in addition to the presence of highly soluble cell wall components such as fats, fatty acids, fatty alcohols, phenols, terpenes, resin acids, and waxes (Kristova et al 1998).

There was a notable association between the effects of temperature and time on the pulp yields. For instance, relatively similar pulp yields were obtained for experiments 4 and 9 (40.69 and 40.02%) and 6 and 11 (38.62 and 36.36%) respectively. Similar results were also obtained for their residual lignin contents. The same pattern is revealed all through Table 2. This showed that pulping at low temperature for a longer time resulted in the same pulp yield and residual lignin content with that obtained at high temperature for a short time. Thus, pulping at high temperature is more desirable as it will cause a great reduction (about 80%) in the pulping time for the same degree of cooking. However, when a reduction in energy consumption is desired, pulping should be done at a lower temperature for a longer time.

Liquor to solid ratio (LS)

Increasing the liquor to solid ratio had relatively little effect on the pulp yields compared to the residual lignin, especially at a higher temperature. In fact, the pulp yield only decreased from 40.02 to 36.36% (experiments 9 and 11), while there was no decrease at all from 32.02 to 32.11 (experiments 10 and 12) as the liquor to solid ratio was increased. However, the residual lignin content decreased for the same period of pulping. This was expected, because more reagents were available per unit mass of solid. Thus it could be expected that solubilization increases when more solvent is present, and delignification reaction goes faster due to the high concentration of soda per unit mass of lignin.

Table 2. Pulping Conditions, Pulp Yields, and Residual Lignin of *Carpolobia lutea*

Experiment No	Soda (%)	Ethanol/ Water (%)	Liquor-to-solid ratio	Pulping temper-ature, (^{o}C)	Time-to-tempera-ture (min)	Pulp yield (%)	Residual lignin (%)
1	8	-	7:1	150	30	43.18	4.46
2	8	-	7:1	150	150	34.53	3.00
3	8	60/40	7:1	150	30	48.53	4.62
4	8	60/40	7:1	150	150	40.69	4.54
5	8	60/40	10:1	150	30	45.83	6.10
6	8	60/40	10:1	150	150	38.62	3.78
7	8	-	7:1	170	30	34.53	2.77
8	8	-	7:1	170	150	27.11	1.27
9	8	60/40	7:1	170	30	40.02	4.36
10	8	60/40	7:1	170	150	32.02	2.02
11	8	60/40	10:1	170	30	36.36	3.47
12	8	60/40	10:1	170	150	32.11	1.03
13	12	-	7:1	150	30	31.85	4.34
14	12	-	7:1	150	150	27.27	1.86
15	12	60/40	7:1	150	30	39.00	4.50
16	12	60/40	7:1	150	150	33.14	2.52
17	12	-	7:1	170	30	30.16	1.63
18	12	-	7:1	170	150	20.65	1.24
19	12	60/40	7:1	170	30	34.10	2.76
20	12	60/40	7:1	170	150	29.24	1.05

The Factorial Design

The experimental design together with the pulp yield and the residual lignin are presented in Table 3. Experiments 1 to 15 of Table 3 allowed the calculation of different parameters a_i and a_{ij} in equation 1, based on the regression analysis. These were subsequently subjected to a t - test to check their significance at 90 to 95% confidence

level. A series of experiments were used around a central point of experiments to estimate the first and second order interaction terms of the polynomial. Experiment 9 of Table 3 is the central point of the design and corresponds to the following reaction conditions:

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

Table 3. Experimental Design and Result for Pulp Yield and Residual Lignin

Experiment No.	X_1 Temperature	X_2 Concentration	X_3 Time	Yield (%)	Lignin (%)
1	1	1	1	29.24	1.05
2	-1	1	1	33.14	2.52
3	1	1	-1	34.10	2.76
4	-1	1	-1	39.02	4.50
5	1	-1	1	32.03	2.02
6	-1	-1	1	40.69	4.54
7	1	-1	-1	40.02	4.36
8	-1	-1	-1	48.53	4.62
9	0	0	0	31.28	1.70
10	1	0	0	39.23	3.59
11	-1	0	0	37.21	3.25
12	0	1	0	32.13	1.73
13	0	-1	0	31.10	1.69
14	0	0	1	40.28	3.39
15	0	0	-1	37.54	1.78

All normalized independent variables for the central points of the design are zero. The dependent variables (pulp yield and residual lignin) were related to the independent variables through the following equations:

$$\text{Pulp yield} = 36.37 - 3.50X_1 - 3.17X_2 - 3.40X_3 \quad (r^2 = 0.95;\ F > 23.54;\ \text{Sig. F (\%)} > 99) \quad (3)$$

$$\text{Residual lignin} = 2.9 - 0.64\,X_1 - 0.76\,X_2 - 0.79\,X_3 \quad (r^2 = 0.80;\ F > 5.35;\ \text{Sig. F (\%)} > 95) \quad (4)$$

Values calculated from the respective polynomial equations were plotted with the experimented results for the different response variables as shown in Figs. 1 and 2. The results showed good correlation between experimented values and those predicted by the models with errors less than 6% for the pulp yield and 20% for the residual lignin.

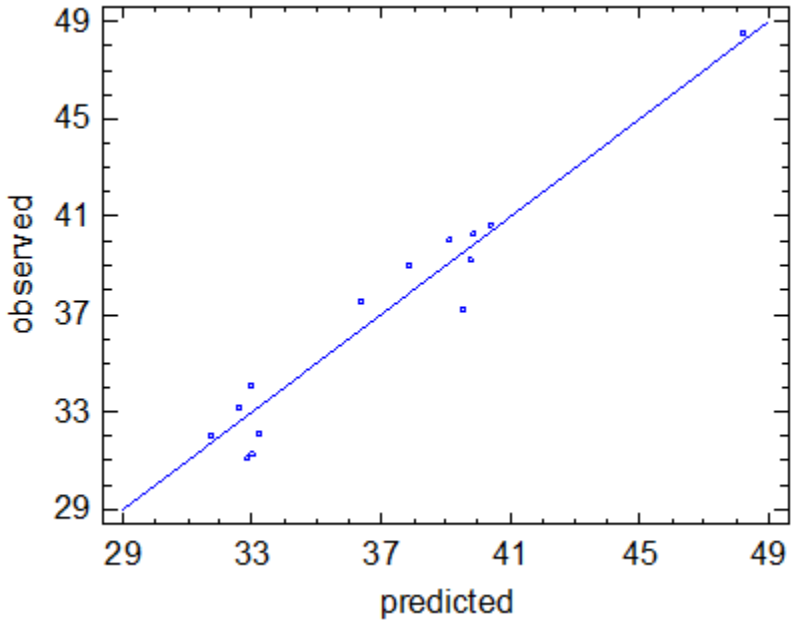

Figure 1. Correlation of the observed and predicted value of the pulp yield

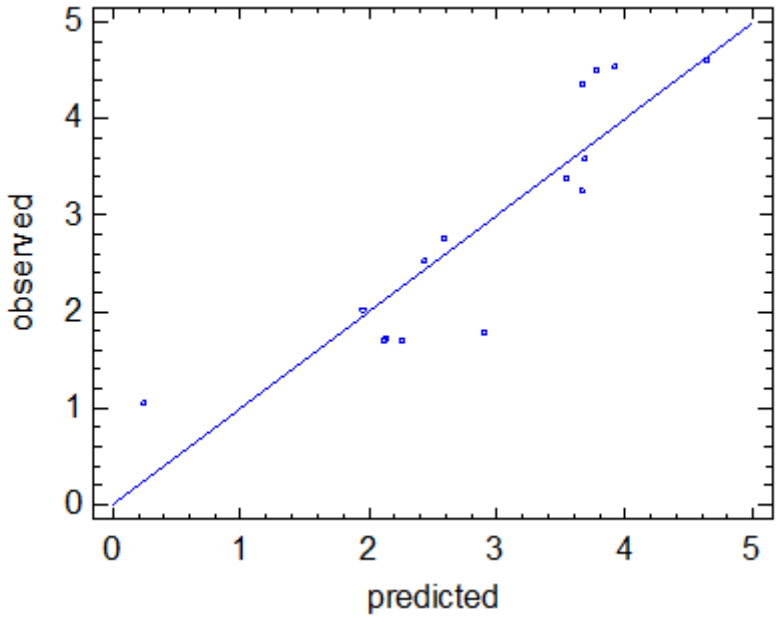

Figure 2. Correlation of the observed and predicted value of the residual lignin

Figure 3 shows the estimated soda-ethanol pulp yield as a function of temperature and concentration, at a constant low value of time. The height of the surface represents the value of pulp yield. According to equation 3, the highest obtainable yield was 46.44%, which occurred at low values of the process variables (-1 for all). The minimum variation in the highest pulp yield was caused by changes in the concentration of the

cooking liquor (change of 6.34 units), while the maximum variation was caused by changes in both temperature (change of 7.0 units) and time (change of 6.8 units), respectively, as observed in the coefficients of X_2 and X_3 of equation 3, and as shown in Fig. 3. The lowest pulp yield (26.3%) was obtained at large values of the three process variables (i.e. +1 for all). This yield could be raised to about 30.0% by pulping at a lower temperature and/or reduced time (-1 normalized value). Pulping at a lower temperature would result in some savings in energy consumed in addition to increasing the pulp yield.

The minimum lignin content of the soda pulp according to equation 4 was obtained at high values of cooking time, temperature, and concentration. The variation of lignin with time and temperature at a medium concentration of cooking liquor is shown in Fig. 4. Accordingly, the highest variations in the minimum residual lignin content was caused by changes in time (1.58 units), while the lowest variation was caused by temperature (1.28 units). Changes in concentration of cooking liquor (1.52 units) fall in between.

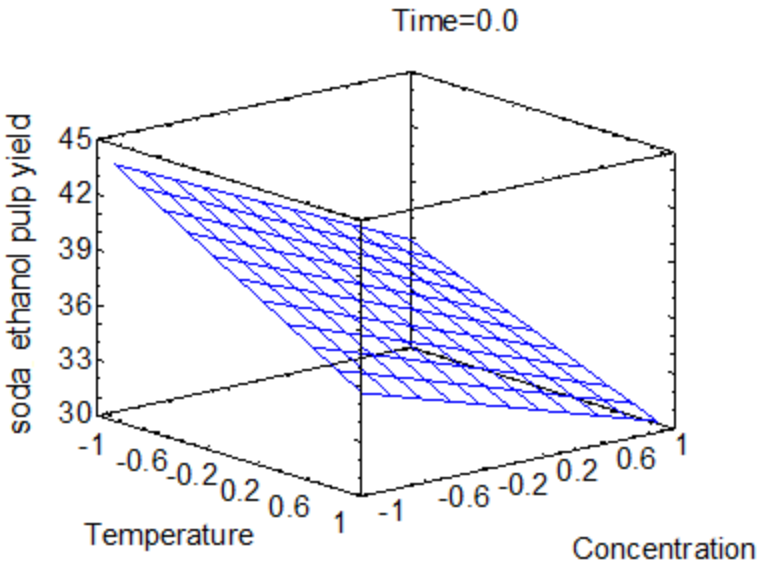

Figure 3. Variation of pulp yield with temperature and concentration

Selectivity of Lignin Dissolution

The selectivity of the dissolution of lignin content is illustrated in Fig. 5. The selectivity of *Carpolobia lutea* lignin by the soda-ethanol process was expressed as the logarithm of the product of the yield and residual lignin versus the logarithm of residual lignin, after the method of Masura (1993). The result showed that the preferential dissolution of lignin over carbohydrate was independent of the working condition. Relatively high correlation between variables was observed, indicating that quantitative estimations could be established between the yield and residual lignin content within the range studied.

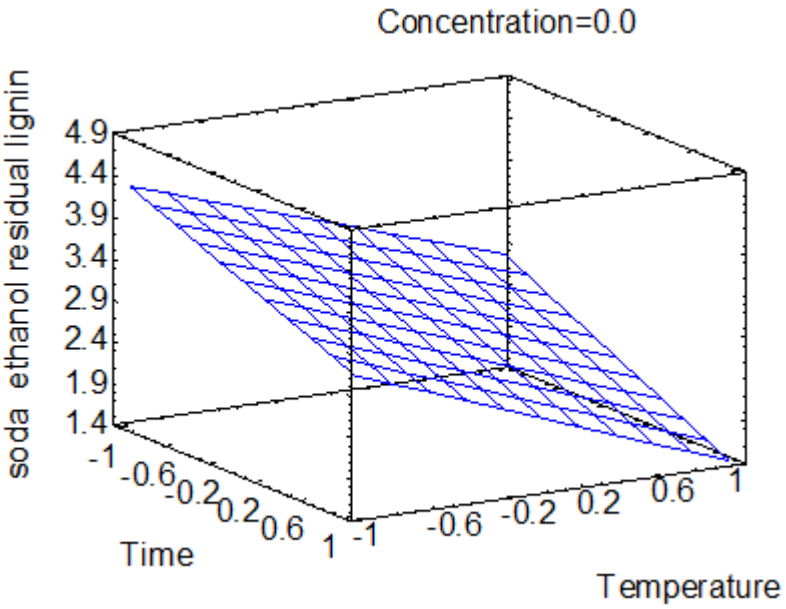

Figure 4. Variation of residual lignin with time and temperature

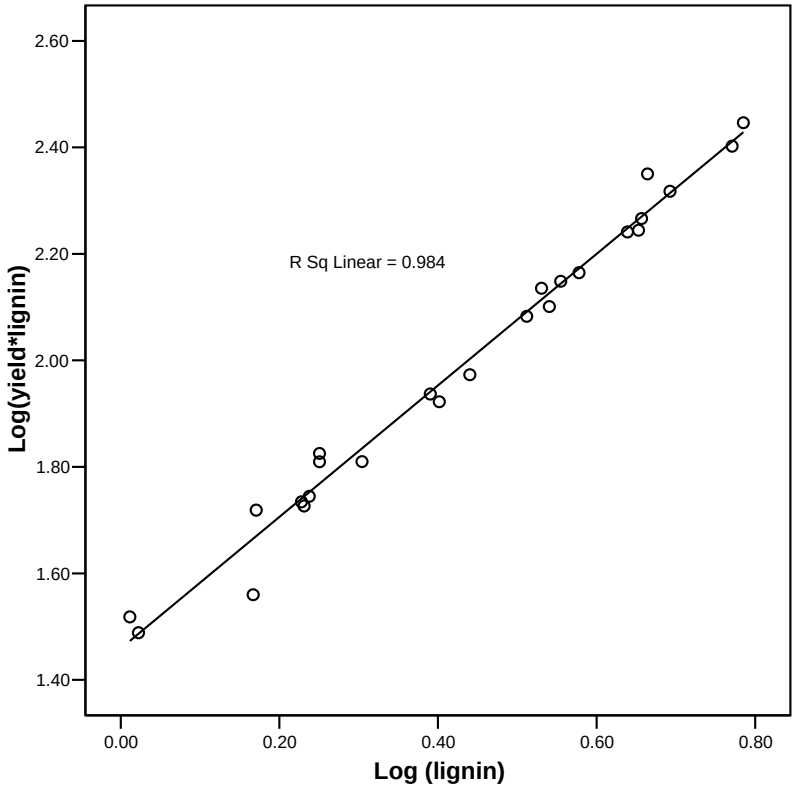

Figure 5. Selectivity graph for the soda-ethanol pulping of *Carpolobia lutea*

Ratio of Dissolved Lignin to Weight Losses

The ratio of the dissolved lignin to the weight losses has been used to estimate the quantity of lignin present in a given pulp of known yield (Iglesias et al. 1996). As shown from Table 4, the ratio ranged from 0.35 to 0.42 with an average of 0.37 and 0.36 at 30 and 150 minutes of cooking respectively. The relatively close values seem to suggest that solubilization and delignification take place at the same rate.

Table 4. Ratio of Dissolved Lignin to Weight Losses

Concentration	Liquor to solid ratio	Temp. (^{o}C)	Time (minutes)	
			30	150
8	7:1	150	0.42	0.36
8	7:1	170	0.36	0.35
8	10:1	150	0.37	0.36
8	10:1	170	0.35	0.37
12	7:1	150	0.35	0.35
12	7:1	170	0.35	0.35
		Average	0.37	0.36

CONCLUSIONS

1. The chemical properties of *Carpolobia lutea* revealed that it is similar to most non-wood fiber materials.
2. Addition of ethanol to the soda cooking liquor increased both pulp yields and residual lignin contents
3. The maximum variation in the minimum residual lignin content was caused by changes in time, while temperature and time were responsible for the variation in the highest pulp yield.
4. Combined effects of temperature and time revealed that pulping at high temperature for a short time can be more advantageous, especially when a high rate of delignification and substantial savings in time is required.
5. The selectivity of lignin dissolution was independent of the working conditions, while the ratios of the dissolved lignin to the weight losses were relatively constant, suggesting that solubilization and delignification take place almost at the same rate irrespective of the duration of cooking.

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