Monoethanolamine Pulping Of EFB (Agro-Biomass): Effect of Operational Variables on Pulp Screen Yield

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Abstract: **In this research work, pulping trials were carried out using the MEA process. The operating conditions such as 50%, 75%, 100% MEA concentration, 150, 160, 170^{o}C cooking temperature, and 60, 90, 120minutes cooking time at constant 4/1 liquor biomass ratio were investigated systematically to establish optimal pulping conditions. This paper investigates the effect of operational (independent) variables i.e. cooking temperature, cooking time, and liquor concentration at constant liquor-biomass ratio of 1/4 on pulp screened yield (dependent variable). By using a central composite factorial design (CCD), equation relating the dependent variable to the different independent variables was derived; which reproduced the experimental results for the dependent variable with errors less than 15%. The lignin content of EFB (18.29%) was low; indicating that EFB should be easier to pulp. The optimum cooking conditions for MEA pulping were 75% MEA concentration, 90 minutes cooking time, and 150°C cooking temperature. The laboratory-scale experimental results indicated that MEA-pulping process is particularly well suited for the pulping of agro-based fibers e.g. EFB of Oil Palm, which was delignified to a low kappa number value of 17.5, pulp yield of 54.73% and screen yield of 53.27% recording a reject of only 1.46%, indicating a good alternative to the Kraft pulping process because of its less polluting effect (environmental impact).**

Keywords: **Pulp Screened Yield; EFB of Oil Palm; Lignin, MEA-pulping, Kraft, Central Composite Design (CCD) .**

I. INTRODUCTION

The chemical pulping strategies can be classified into two major principles namely; alkaline such as kraft process and soda process and acidic such as sulfite and bisulfite process. The kraft process is a modification of the soda process which utilizes sodium hydroxide (NaOH) with the addition of sodium sulfate (Na_2SO_4) into the cooking liquor *system (Sjostrom, 1993; Smook, 1992).* Sulfite pulping is a solubilization of lignin from cellulose as salts of lignosulfonic acid using mixtures of sulfurous acid (H_2SO_3) while bisulfite pulping uses bisulfite ion (HSO^{-3}) **(Casey, 1980; Smook, 1992)**. Besides, sulfite pulping also can be carried out in neutral and alkali medium and known as neutral and alkaline sulfite processes **(Smook, 1992)**. Kraft pulping is always associated with severe environment pollution especially air pollution. The air pollution from the kraft pulping is a major concern with the emission of sulphur gases into the atmosphere with a rate of 0.3-3 kilograms per metric tonne (kg/t) of air-dried pulp (ADP*) (World Bank Group, 1998).* The four reduced sulphur gases are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. Obnoxious gaseous odor are released even from the advanced kraft mills. All the gases have extreme low odor thresholds, which indicated that long term exposure to these gases can cause imbalance in ecosystem and even human health will be seriously interfered *(Smook, 1992; Casey, 1980).* Due to the awareness towards the negative impact of kraft mill's effluent to the environment recently, soda pulping started to regain its popularity among the pulp mills especially non-wood based pulp mills after it had been abandoned since 1930s *(Smook, 1992).* As indicated by *World Bank Group (1998),* the production of 1 tonne of air dried pulp, generated 10-40 kg of BOD and 20-200 kg of COD. Besides, considerable high total suspended solid (10-15 kg per tonne air dried pulps) also has been reported. The high discharge of COD consumes oxygen, depletes that actually available to fauna and flora, thus damaging the ecosystem near effluent discharged. High levels of suspended solids from the pulp mill effluent can also cause problems of both water opacity and blanketing of river or lake beds. Severe blanketing may also result in anaerobic decomposition under the blanket where hydrogen sulfide will be released into the aquatic ecosystem. Organic solids can also absorb many of the toxins presents in mill effluents, such as resin and fatty acids and heavy metals. This can have long-term effects over a wider area as a result of bioaccumulation and transportation through the food chain *(Stanley, 1996).*

Both humans and the environment are continuously exposed to chemicals. The impact of effluent discharged from the chemical pulp mills into the receiving water has roused the awareness of the public on the damaging effects these chemical substances have on living organisms. Major challenges in this area concern reducing emissions and the

spread of environmentally hazardous chemicals by developing alternatives to the use of particular chemicals thus, exerts pressure on the pulp and paper mills to develop and adopt environmental friendly process technology for the production of pulp and paper *(Chibudike, 2019).*

Technology for pulp and paper production has advanced considerably and efforts are being made to reduce environmental impact of pulp and paper production processes through the use of organosolv pulping method developed to avoid environmental problems related to Sulphur emissions. In several countries of the world as it applies to Nigeria, precisely in the Pulp and Paper Research Technology Division of the Federal Institute of Industrial Research, Oshodi (FIIRO), kraft method had been the dominant pulping process and the dominance of the kraft process was anchored upon its versatility to pulp almost any kind of wood successfully. But prominent are the emissions of some fowl smelling and malodorous pollutant associated with the pulping process such as mercaptans, p-cymols, and chlorinated organic compounds etc. In 2012, this method was substituted by the soda process because it is less polluting compared to the kraft process, but the fact remains that the soda process is still faced with severe drawbacks. Strongly alkaline cooking liquors dissolve carbohydrates to a great extent with negative impact on pulp yield. Most annual plants have a high content of silica, which is dissolved to a high extent in the strongly alkaline cooking liquor and thus creates serious problems in the evaporators, the recovery boilers and in the causticizing plant. These are the main reasons why soda pulping black liquor handling and recovery of chemicals is still problematic **(***Chibudike et, al. 2011).*

When monoethanolamine (MEA) was investigated as the main delignifying agent, a different scenario was observed. Monoethanolamine (MEA) has several advantages when compared with other popular methods such as kraft or sulfite pulping which includes high selectivity of MEA resulting in pulps with high yields, low kappa numbers and acceptable strength properties. In particular, the ability to obtain relatively high quality lignin adds value to a process stream otherwise considered as waste. Organic solvents are easily recovered by distillation, leading to less water pollution and elimination of the odor usually associated with Soda and kraft pulping.

The objective of this research work was to develop an eco-friendly and energy saving biomaterials and processes that would lead to implementation of sustainable manufacturing strategies.

II. EXPERIMENTAL MATERIALS

In this research work, Nigeria-grown Agro-based Fibers (Empty Fruit Bunch of Oil Palm) generated during post-harvest treatment of Oil Palm Fruit Bunches at a palm plantation at Okiti Kpupa, in Ekiti State, Nigeria were used.

Working plan for Bio-mass Fractionation

Figure 1 depicts the working plan. The EFB of Oil Palm was characterized chemically and morphologically, and converted into brown pulp and bleached to a low kappa no. value of 16.2 and 17.9 by the EoP sequence and characterized for their beatability, drainability and physical-mechanical properties.

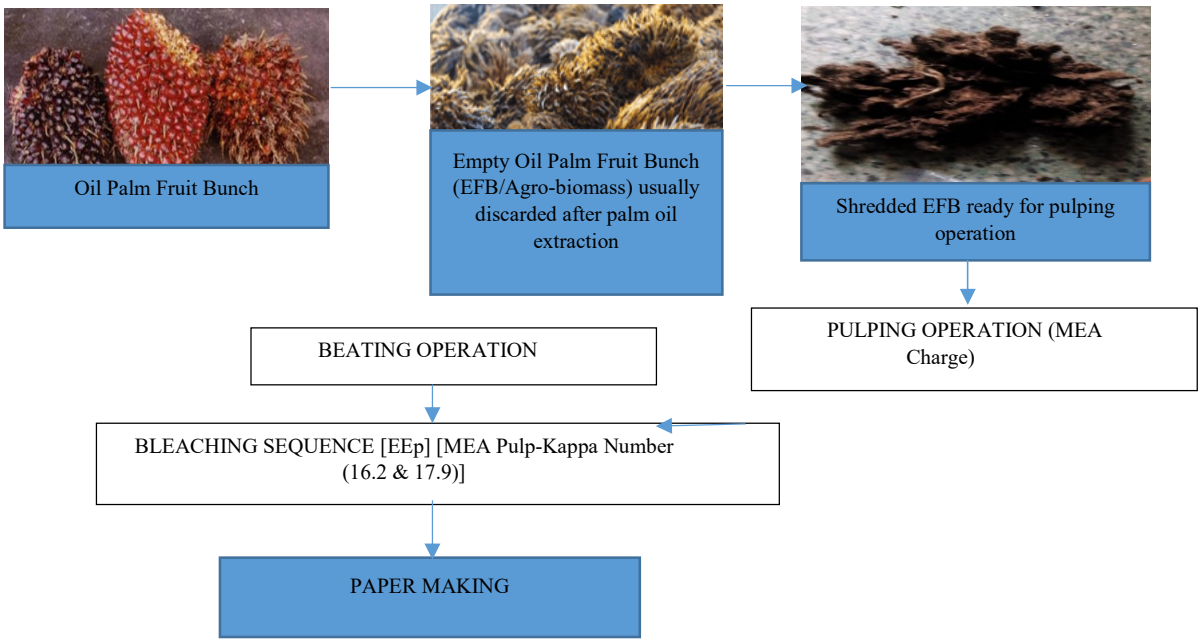

Figure 1: Working plan for EFB (Agro-biomass) conversion to Pulp & Paper

Experimental design for the pulping conditions

The pulping experimental design considered the following factors are described in table 1.

Table 1: Concentrations of Cooking Liquor, Pulping Temperatures and Cooking periods

Experimental Conditions	Monoethanolamine (MEA) Process		
	MEA Charge (%)	Maximum Temp. (°C)	Maximum Cooking Duration (minutes)
Factor 1	50	150	60
Factor 2	75	160	90
Factor 3	100	170	120

The experimental design had 27 treatments (3×3×3) = 27 and 2 replicates

Monoethanolamine (MEA) pulping

After a thorough cleaning process, 2kg of air-dry sample was loaded into a 15 L capacity batch reactor (digester) with eight (8) liter cooking liquor at liquor-sample ratio of 4:1. The digester mounted in the Pulp and Paper Research Laboratory of the Federal Institute of Industrial Research, Oshodi, (F.I.I.R.O.), lagos-Nigeria is furnished with an outer electrical heating jacket. The lid of the digester was firmly bolted to prevent leakage, the digester was switched on and the time of rise of temperature and pressure was noted at intervals of five (5) minutes. The content of the digester was stirred while in operation by rotating the vessel via a motor connected through a rotary axle to a control unit, including measurement and control instruments of pressure and temperature, to facilitate attainment of the working temperature (5°C/min). The pulping temperatures gradually rose and allowed to be steady at varying maximum temperatures of 150, 160 and 170oC. The digester was switched off after varying maximum cooking periods of 60, 90 and 120 minutes from start of operation and allowed to cool below 60°C before the content were blown down. The digester's initial temperature, pressure and starting time were all noted, and the various changes in these parameters were also recorded. The resultant pulp was subjected to thorough washing with plenty of water. When it was observed that subsequent washing resulted in no further change in color, the pulp was transferred into the valley beater for processing into a more refined pulp.

Screening of EFB Pulp Samples Cooked sample chips were put through the screening machine. Only acceptable size of the sample fiber passed through the screen plate and the rejected or oversized fiber were left on the screen plate. This process is crucial in papermaking to ensure smooth and uniform paper texture. Pulp yield was determined in accordance with TAPPI standards T-257.

Table 2: Experimental Conditions for the Pulping Process

MEA Pulping Condition	Conditions of Cooking Operation Showing Values of Independent Variables
Air dry weight of EFB (kg) (A.D)	2
Ratio of liquor/biomass	4:1
Maximum temperature (°C)	150, 160, 170
Time to reach maximum temperature (minutes)	51
Time at maximum temperature (minutes)	9, 39, 69
Liquor charge (%)	50, 75, 100
Over-all cooking time (minutes)	60, 90, 120

IV. RESULTS AND DISCUSSION

All analytical tests were carried out in duplicate. Statistical analysis was performed using the Design Expert software. Data were analyzed by the analysis of variance (ANOVA), and p-value lower than 0.05 was considered significant in surface response analysis. The optimal values of the operation parameters were estimated by the three-dimensional response surface analysis of the independent variables (Cooking temperature, Cooking time and Liquor charge respectively) and the dependent variable (Pulp Yield =Y%).

Statistical Interpretation of Data

In this study a Central Composite Design (CCD) with three independent variables was applied to investigate the effect of Cooking temperature, Cooking Time and liquor charge/concentration at constant liquor to biomass ratio of 4 to 1 on the Pulp Screened. The results of the analysis of variance (ANOVA) are summarized to test the soundness of the model.

Table 3: Experimental Conditions used in the MEA Pulping of EFB investigated

Exp. No.	Independent variables			Dependent variables
	Cooking Temp. (°C)	Cooking Time (mins)	MEA % (D.W.)	Pulp Screened Yield (%)
1	150	60	50	45.43±1.8
2	150	90	50	48.97±4.5
3	150	120	50	42.11±2.5
4	160	60	50	43.67±4.6
5	160	90	50	47.77±3.6
6	160	120	50	44.87±3.4
7	170	60	50	40.67±4.1
8	170	90	50	42.54±2.0
9	170	120	50	43.33±0.5
10	150	60	75	47.88±1.1
11	150	90	75	50.27±1.7
12	150	120	75	45.78±1.6
13	160	60	75	46.87±2.3
14	160	90	75	49.95±2.1
15	160	120	75	44.56±0.5
16	170	60	75	47.55±1.5
17	170	90	75	49.99±3.4
18	170	120	75	45.23±0.4
19	150	60	100	47.30±1.4

20	150	90	100	48.79±0.5
21	150	120	100	41.12±1.7
22	160	60	100	43.24±1.9
23	160	90	100	44.44±2.1
24	160	120	100	39.97±8.2
25	170	60	100	40.09±3.2
26	170	90	100	39.67±5.3
27	170	120	100	36.89±1.8

The mean squares values were calculated by dividing the sum of the squares of each variation source by their degrees of freedom, and a 95% confidence level (= 0.05) was used to determine the statistical significance in all analyses.

Table 4: Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	43099.11	1	43099.11			Suggested
Linear	15.94	3	5.31	0.87	0.4750	
2FI	4.88	3	1.63	0.23	0.8746	
Quadratic	64.97	3	21.66	7.90	0.0054	Suggested
Cubic	25.46	7	3.64	5.55	0.0936	Aliased
Residual	1.97	0.0936				
Total	43212.33	3	0.66			
		20	2160.62			

Table 5: Model Summary Statistics

Std. Dev.	1.66	R-Squared	0.7578
Mean	46.42	Adj R-Squared	0.5398
C.V.	3.57	Pred R-Squared	-0.0871
PRESS	123.08	Adeq Precision	6.861

Table 6: ANOVA for Response Surface Quadratic Model [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	85.80	9	9.53	3.48	0.0326	significant
A	10.93	1	10.93	3.99	0.0738	
B	7.22	1	7.22	2.63	0.1357	
C	1.25	1	1.25	0.45	0.5155	
A^2	1.66	1	1.66	0.61	0.4540	
B^2	39.37	1	39.37	14.36	0.0036	
C^2	30.71	1	30.71	11.20	0.0074	
AB	0.27	1	0.27	0.098	0.7604	
AC	0.90	1	0.90	0.33	0.5802	
BC	6.33	1	6.33	2.31	0.1596	
Residual	27.42	10	2.74			
Cor Total	113.22	19				

R^2 value of 0.7578 is the percentage of the dependent variable variation explained by the linear model. It indicates slight variation of pulp yield data around it mean as explained by the linear quadratic model. A negative "Pred R-Squared" value of -0.0871 implies that the overall mean is a better predictor of pulp screened yield than the current model. "Adeq Precision" compares the range of the predicted values at the design points to the average prediction error. The ratio of 6.861 indicates an adequate signal that this model can be used to navigate the design space.

The Model F-value of 3.48 implies the model is significant. Values of "Prob > F" greater than 0.1000 indicate the model terms are not significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B^2, C^2 are significant model terms. . The residual row shows how much variation in the response is still unexplained which from the Table 6 presented, the variation is insignificant. Same goes for Lack of Fit, Pure error and Cor Total.

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Coded Factors (equation 1):	
Pulp Screened Yield	
+49.24	
-1.14	* A
-0.92	* B
-0.46	* C
+0.65	* A^2
-3.16	* B^2
-3.10	* C^2
+0.23	* A * B
+0.52	* A * C
-1.37	* B * C

Final Equation in Terms of Actual Factors (equation 2):	
Pulp Screened Yield	
+204.65350	
-2.41306	* Cooking Temp.
+0.61784	* Cooking Time

+0.55927	* MEA Concentration
+6.49027E-003	* Cooking Temp.^{2}
-3.50740E-003	* Cooking Temp.^{2}
-4.95638E-003	* MEA Concentration^2
+7.50949E-004	* Cooking Temp. * Cooking Time
+2.06776E-003	* Cooking Temp. * MEA Concentration
-1.83213E-003	* Cooking Time * MEA Concentration

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels are already specified in the original units for each factor.

Therefore, the second-order polynomial model equation 1 is expressed as follow:

Pulp Screened Yield = +49.24 – 1.14A – 0.92B - 0.46C +0.23AB + 0.52AC – 1.37BC +0.65A² - 3.16B² - 3.10C²

According to the monomial coefficient value of regression model Equation presented above, X_1 = A = -1.14 (Cooking Temperature), X_2 = B = -0.92 (Cooking time) and X_3 = C = -0.46C (MEA concentration), and the order of priority among the main effect of impact factors is Liquor (MEA) Concentration (X_3) > Cooking Time (X_2) > Liquor (MEA) concentration (X_1).

Diagnostics of the Linear Regression (Quadratic) Model

The residuals are represented graphically by means of a residual plot as shown in figure 2. This normal probability plot indicates whether the residuals follow a normal distribution, thus follow the straight line. Here, the scatter had a definite pattern along the straight line which indicates that a transformation of the response may provide a better analysis.

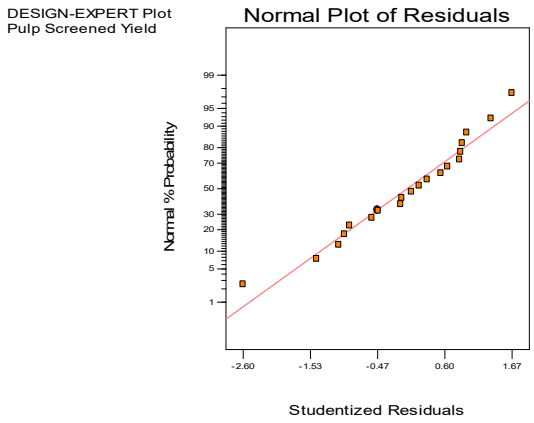

Fig. 2: Normal Plot of Residuals for MEA Process

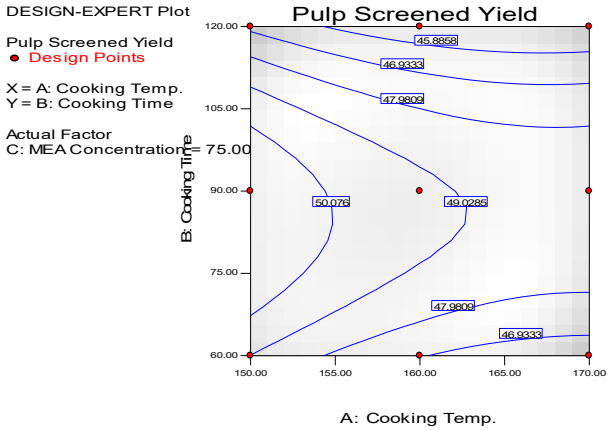

Fig. 3: Model Graph of Pulp Screened Yield for MEA-Process

Numerical optimization uses the models to search the factor space for the best trade-offs to achieve multiple goals, while *Graphical optimization* uses the models to show the volume where acceptable response outcomes can be found. In order to specify the best cooking conditions so as to maximize the potentials of the monoethanolamine pulping process, the data generated from the pulping operations were subjected to optimization analysis using Design Expert Software 12 and results are presented in Table 7.

Table 7: Optimization (Numerical & Graphical) of the pulping conditions using Design Expert 12 Software

Solutions Number	Cooking Temp.*	Cooking Time*	MEA Concentration	Desirability	
1	*159.90*	*104.35*	*89.38*	1.000	Selected
2	*157.82*	*93.55*	*97.03*	1.000	
3	*153.49*	*104.05*	*79.20*	1.000	
4	*150.23*	*96.34*	*63.45*	1.000	
5	*154.29*	*75.08*	*98.86*	1.000	
6	*158.43*	*79.97*	*51.91*	1.000	
7	*161.67*	*91.41*	*89.87*	1.000	
8	*164.70*	*61.32*	*61.23*	1.000	
9	*166.65*	*98.73*	*97.55*	1.000	
10	*156.89*	*65.99*	*96.21*	1.000	

In order to select the optimum parameters for the pulping conditions maximizing pulp yield and minimizing all possible constraints, design expert presented a range of solution (10) choices presented in Table 7 above, which were compared to determine which might be "best" in terms of considering all possible advantage/benefit (minimal cost, maximal profit, minimal error and optimal design) with the goal of understanding and resolving the modelling issue (ensuring the model fit and the data fit perfectly).

From the results of the optimization analyses conducted 10 Solutions were found and the best solution is selected as presented in Table 7

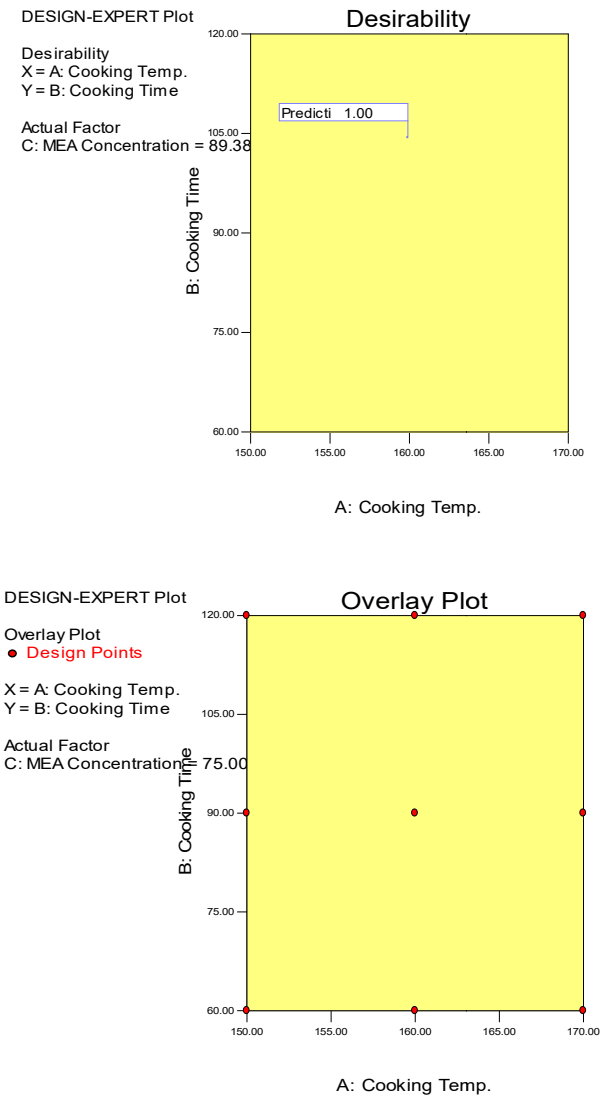

Figure 4: Numerical and Graphical Optimization solution for the Pulping Conditions

Figure 5: Showing unbleached EFB Pulp Samples and Pulp Sheets from MEA Process

Figure 6: Showing EFB Pulp Samples from MEA Process Bleached to 16.2 Kappa Number and Pulp sheets

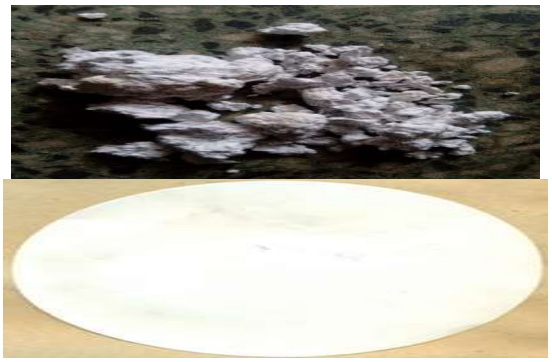

Figure 7: Showing EFB Pulp Samples from MEA Process Bleached to 17.5 Kappa Number and Pulp Sheets

Yield of EFB from MEA Pulping Process at a maximum cooking temperature of 150°C, maximum cooking time of 90 minutes and with pure 75% MEA furnished 50.27±1.7% and this is a clear indication that sufficient delignification was achieved. The main focus laid on reduction in the MEA charge by partial substitution with water. A MEA/water ratio of 75/25 was successfully applied, furnishing a pulp screened of 50.27. Under these conditions a kappa number range of 16 to 18 was attained which means the pulp is still bleachable. Comparing the pulping potentials of MEA process with conventional process like soda, it was observed that MEA pulping process furnished higher pulp yield at lower kappa number investigated.

Further Work

Another focus of this research in future would be directed on the reduction of the cooking temperature. To enhance the pulping operation in order to maximize pulp screened yield for this process, the monoethanolamine cooking operation need to be catalyzed. This would be carried out in the next stage of this research work using the following experimental condition: Cooking Time =104.35minutes; Liquor (MEA) Concentration =89.38 at reduced temperature.

V. CONCLUSION AND RECOMMENDATION

When brightness is not crucial or no bleaching is required, but a stronger pulp is desired, one can focus on obtaining a high holocellulose content and an appreciable yield. If such a content is to be only 10% lower than optimum value, using a

high Monoethanolamine concentration (75%), a short cooking time and a low liquid/solid ratio requires employing a temperature of 150^{o}C in order to obtain a yield, holocellulose content, lignin content, and kappa number of 50-55, 75-85, 10-18 and 15-20%, respectively. If one also desires to ensure reasonable strength in the pulp and highly efficient use of the raw material, then the yield and holocellulose content should reach preset thresholds, and the lignin content and kappa number should be as low as possible. Thus, the yield and holocellulose content can only be allowed to decrease by 15% at most from their optimum value, and a moderately high MEA concentration and low liquid/solid ratio should be used to obtain a yield, holocellulose content, lignin content and kappa number of 51-56, 79-84, 14-22, and 16-20%, respectively, with a temperature, time, and MEA concentration of 145-155^{o}C, 60-90 minutes, and 70-80%, respectively. The pulp thus obtained is acceptably strong (possessing a high holocellulose content) and is easily bleached (thanks to its low lignin content and kappa number); the raw material is inefficiently used (the low yield obtained is typical of chemical pulp), but the short time and small amount of raw material used result in immobilized capital savings and it has favorable effects also on reagent recovery from the black liquor.

Delignification by use of monoethanolamine (MEA) is an innovative, environmental friendly chemical pulping process that works without the use of sulphur compounds, with a particular benefit of simple MEA recovery by distillation, allowing black liquor combustion to be dispensed and the dissolved lignin recovered. The MEA process is suitable for pulping both hardwood and softwood. Compared with conventional processes, the MEA process has the advantage of achieving a high degree of delignification through an increase in temperature during pulping without damage to the cellulose. MEA pulping is none polluting process compared with the soda process which is associated with heavy pollution load.

The search for local long fiber pulp material which can be easily propagated remains one of the most important key desirderatum for the eventual resuscitation of the present mom bund paper industries of Nigeria. One important way of stemming the tide of imports is to find a good substitute to fine pulp for the use of the Nigeria paper companies when they eventually start producing. Besides being an innovation and new entry into the pulp map, the EFB fiber can become the best gift of FIIRO into the future pulp market of the tropical world.

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