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Research Article

OPTIMIZATION OF PULP YIELD FOR CATALYZED-MEA CONVERSION OF AGRO-WASTES TO PAPER-PULP

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Abstract

This paper investigates the suitability of Catalyzed-MEA pulping of agro-biomass (empty fruit bunches), viewed as alternative raw material for pulp and paper production. In this research work, the effect of three (3) pulping additives (anthraquinone, polysulfide and surfactant) used in the monoethanolamine pulping of agro-biomass, their possible interactions and the influence of operational variables on pulp yield were investigated. The agro-fibers were cut in bits and pulped using a biomass digester. For the pulping process, a 15litre capacity rotating type wood digester was used to pulp 1000 o.d. g of biomass considering the best pulping conditions investigated in previous research study (cooking temperature =125±2oC, cooking time =77.783minutes, liquor concentration=87.493%, and liquor/biomass ratio=4.832/1) that furnished the best pulp yield. The lid of the digester is attached at the top with measuring devices of temperature and pressure with careful consideration of other factors to ensure the cooking conditions are strictly adhered to. The cooking operation of the digester was designed so that the experimental conditions considered the following factors and levels: Factor 1: 0, 0.25 and 0.5% Surfactant charge, Factor 2: 0, 2 and 4% polysulfide charge, Factor 3: 0, 0.25 and 0.5% anthraquinone. The experimental design had 27 treatments (3×3×3) and 2 replicates. In this research, a non-ionic commercial surfactant was used; the polysulfide was generated by the addition of sulfure to the hot white liquor (80oC) under agitation until complete dissolution. By using a central composite factorial design, equations relating the dependent variable (pulp yield) to the different independent variables (surfactant, polysulfide and anthraquinone concentration) were derived; reproducing the experimental result for the dependent variable with errors less than 15%. The pulp yield range (42.12-53.17%), Kappa number (10.8-34.3), viscosity (382-849 ml/g) and brightness (65.7-90.6%). This is an indicative of the fact that the cellulosic pulp materials are averagely appropriate for high-brightness printing papers. It is also recommended that the cellulosic pulp obtained from the MEA process as virgin fiber is suitable for strengthening secondary fibers in recycled papers and also for developing certain types of writing, printing and packaging paper materials.

Keywords: Agro-wastes, PulpYield, Catalysed-MEA pulping, Surfactant, Polysulfide, Anthraquinone, EFB of Oil Palm.

INTRODUCTION

The first published work concerning applications of EFB was that of Muthurajah and Peh (1977), who used the kraft process with a concentration of active alkali 16%, for 3 hours at 160°C, obtaining a pulp with a yield of 56% and a kappa number of 16.9. The chemical properties of EFB fibers are similar to those of hardwood, except for the pentosan content, which is higher. Subsequently, the kraft process has also been studied by other authors (Akamatsu *et al.* 1987a; Khoo and Lee 1991; Ibrahim 2002). Ibrahim (2002) compared the composition of EFB pulp obtained by the kraft, kraft-anthraquinone, soda, and soda-anthraquinone processes; the pulp obtained with the soda process had the highest content of lignin, holocellulose and α-cellulose and a higher viscosity. The soda process has also been studied by Law and Jiang (2001), producing fibers with more wall thickness, greater rigidity, higher solubility in hot water and 1%-soda, as well as a higher ash content. 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.

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In several countries of the world as it applied in F.I.I.R.O, kraft method was the dominant pulping process right from the inception of the pulp and paper laboratory in 1956 up till year 2011. 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. 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). The situation is completely different when monoethanolamine (MEA) as the main delignifying agent was investigated. Delignification by use of monoethanolamine (MEA) is an innovative, environmentally 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. Besides

engineering pulping process modifications, the use of chemical additives at the pulping process represents an interesting possibility to reduce kappa number and increase pulp yield. Among those chemical products are anthraquinone, polysulfide and surfactants. In Sweden, Brazil, Spain and other countries, some of those additives are used individually by some pulp mills. The conjunct use of the mentioned pulping additives is an aspect that should be carefully evaluated in terms of technical and economic feasibility since they have different functions at the pulping process; their conjunct use can show synergistic and beneficial aspects for the pulping process in global terms. The effect of anthraquinone, polysulfide and surfactant on the MEA pulping are not well established and there is a need for specific research (Chibudike, 2019). The objective of this research work is to evaluate the effect of anthraquinone, polysulfide and surfactant charges and their conjunct use on the MEA pulping of agro-base fiber.

EXPERIMENTAL

Materials

In this research, Nigerian cultivated agro-based fibers (EFB and kenaf) were used. EFB of Oil Palm was collected from a palm plantation at Okiti Pupa in Ekiti State, Nigeria. The raw material (EFB) was shredded and dried to about 85% dryness in an acclimated room (23.0 ± 1.0oC and 50.0 ± 2.0% moisture) and stored in polyethylene bags for further use. In terms of additive, powder anthraquinone and a non-ionic commercial surfactant were used, the polysulfide was generated by the addition of sulfur to the hot white liquor (80^{o}C) under agitation until its complete dissolution.

Table 1. Experimental Conditions for the MEA –pulping

Parameters	Levels
MEA Charge (%)	77.783
Maximum Cooking Temperature (oC)	123±5
Maximum Cooking Time (Minutes)	87.493
Heating Time (Minutes)	47
Liquor/Biomass Ratio	4.832:1
Anthraquinone charge (% on o.d. biomass)	0, 0.25 and 0.5
Polysulfide charge (% on o.d. biomass)	0, 2, and 4
Surfactant charge (% on o.d. biomass)	0, 0.25 and 0.5

Methods

Air dried samples of 1000g EFB was cut into about 2 cm long pieces and washed with water to remove adhering soil particles, air dried, and stored with less than 15% moisture content. The sample was loaded into the digester and covered with the cooking liquor (MEA). Conditions of operation used were: 77.783%MEA liquor concentration, 123±5 oC maximum cooking temperature, 4.832/1liquor to biomass ratio and 87.493minutes duration of cooking period. This was based on previous pulping experiments were the aforementioned cooking condition was furnished as the best pulping scenario (optimum cooking condition) out of 27 experimental runs and statistical evaluation. In this research work, the condition of operation that was varied include: anthraquinone (0, 0.25 and 0.5); surfactant (0, 0.25 and 0.5); and polysulfide (0, 2, 4). The lid of the reactor was firmly bolted to prevent leakage. The reactor was switched on and the time of rise of temperature and pressure was noted at intervals of five (5) minutes. The reactor's initial temperature, pressure and starting time were all noted and the various changes in parameters were also recorded. When the cooking process was completed, the digester was switched off, allowed to cool below 60oC and the content removed. 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. This was followed by the bleaching sequence.

RESULTS AND DISCUSSION

As a response, the Pulp Screened Yield was chosen, a total number of 20 best possible pulping scenarios were selected and employed for the response surface modelling (Table 2), and the order of experiments was arranged randomly.

Analysis of Experimental Results

Considering the experimental design, the results were statistically analyzed in order to detect the effect of the additives over the main pulping process variables. 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 time, Liquor charge and Liquor/Biomass Ratio respectively) and the dependent variable (Pulp Yield =Y%).

Model Development and Statistical Interpretation of Data

A total of 20 experiments were found to be sufficient to calculate the coefficients of the second-order polynomial regression model for three variables. The process order here is to develop a quadratic term of a polynomial model, so we import equation 1 and 2 as presented earlier in the former pages of this chapter:

$$Y\% = Ao + A_1X_1 + A_2X_2 + A_3X_3 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 + A_{11}X_{12} + A_{22}X_{22} + A_{33}X_{32} \quad \text{……..... 1}$$

$$Y\% = \frac{A - B}{A} - R \quad \text{……. 2}$$

The behavior of the cooking process is explained by the empirical second order polynomial model. Here Y is the Pulp Screened Yield in %, where A = %Weight of Biomass (before pulping), B= %Weight of Biomass (after pulping) and R= %Weight of Reject.

As described earlier in the previous pages of this chapter, here Ao is the interception coefficient, A_{11}, A_{22} and A_{33} are the quadratic terms, A_{12}, A_{13} and A_{23} are the interaction coefficients, and X_1, X_2, and X_3 are the independent variables studied (Cooking time, Liquor charge and Liquor/Biomass Ratio respectively). Aand B are the percentage weight of Biomass before and after the pulping operation respectively. In Table 3, the results of the analysis of variance (ANOVA) are summarized to test the soundness of the model. Analysis of variance (ANOVA) is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model.

Table 2. Design Layout of Independent Variables (Factors) and the Dependent Variables (Responses) for the Catalyzed Process

Experimental Run	Factor 1	Factor 2	Factor 3	Response 1
	A:Anthraquinone % o.d. biomass	B: Surfactant % o.d. biomass	C:Polysulfide %o.d. biomass	Pulp Screened Yield %
1	0.00	0.00	0.00	49.18
2	0.00	0.00	2.00	48.25
3	0.00	0.25	0.00	49.00
4	0.00	0.25	2.00	51.04
5	0.00	0.50	0.00	49.65
6	0.00	0.50	2.00	50.76
7	0.25	0.00	0.00	50.34
8	0.25	0.00	2.00	50.47
9	0.25	0.25	2.00	50.76
10	0.25	0.25	0.00	50.77
11	0.25	0.50	0.00	49.69
12	0.25	0.50	2.00	50.94
13	0.50	0.00	0.00	48.89
14	0.50	0.00	2.00	50.6
15	0.50	0.25	0.00	49.49
16	0.50	0.25	2.00	50.3
17	0.50	0.50	0.00	49.14
18	0.50	0.50	2.00	50.97
19	0.50	0.50	4.00	48.73
20	0.50	0.00	4.00	47.23

AQ= anthraquinone charge; Surf. = surfactant; PS= polysulfide; TY = total yield; SY: screened yield

Table 3. ANOVA for Response Surface Quadratic Model [Partial sum of squares]

Source	Sum of Squares	Degree of Freedom	Mean Squares	F Value	*P*-Value	Remark
Model	18.07	9	2.01	5.15	0.0091	Significant
A-Anthraquinone-AQ	0.55	1	0.5521	1.42	0.2635	-
B-Surfactant Surf.	3.28	1	3.28	8.41	0.0169	Significant
C-Polysulfide	2.41	1	2.41	6.18	0.0311	Significant
AB	0.79	1	0.79	2.02	0.1968	-
AC	0.38	1	0.38	0.97	0.3351	-
BC	1.71	1	1.71	4.38	0.0617	Significant
A^2	2.44	1	2.44	6.25	0.0330	Significant
B^2	0.57	1	0.57	1.47	0.2623	-
C^2	6.64	1	6.64	17.03	0.0021	Significant
Residual	3.90	10	0.39			-
Lack of Fit		5				
Pure error		5				
Cor Total	65.48	19				
-	$R^2 = 0.8225$	$R^2_{adj} = 0.6628$	-	-	-	

Table 4. Coefficient Table for the Quadratic Model (p-value shading: p<0.05 0.05≤p<0.1 p≥0.1)

	Intercept	A	B	C	AB	AC	BC	A^2	B^2	C^2
Pulp Screened Yield	51.2283	0.303333	0.544619	-0.950972	-0.300143	0.355	0.526095	-0.780833	-0.378333	-1.79653
p-values		0.2616	0.0158	0.0322	0.1855	0.3480	0.0627	0.0314	0.2535	0.0021

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 3 summarizes the Model Statistics of the experimental results presented in Tables 2 and 3.19. R2 value of 0.8225 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. The Predicted R^2 of 0.3378 is not as close to the Adjusted R^2 of 0.6628 as one might normally expect; i.e. the difference is more than 0.2. The Model F-value of 5.15 implies the model is significant. Values of "Prob> F" less than 0.0500 also indicate model terms are significant. In this case B, C, BC, A2, C2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Final Equation in Terms of Coded Factors (Equation 3)

$$\text{Pulp Screened Yield} = +51.23 + 0.30*A + 0.55*B - 0.95*C - 0.78*A^2 - 0.37*B^2 - 1.80*C^2 - 0.3*A*B + 0.36*A*C + 0.53*B*C \quad \ldots\ldots\ldots\ldots 3$$

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 Actual Factors (Equation 4)

Pulp Screened Yield= +48.95661 + 7.24057*Anthraquinone – AQ + 4.30133*Surfactant Surf. +0.880494*Polysulfide - 12.49333*Anthraquinone - AQ^2 - 6.05333* Surfactant $Surf.^2$ - 0.449132* Polysulfide2 - 4.80229*Anthraquinone - AQ*Surfactant Surf. + 0.710000*Anthraquinone - AQ* Polysulfide + 1.05219*Surfactant Surf.*Polysulfide .....….4

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor as summarized in Table 4.

Therefore, the second-order polynomial equation for the catalyzed MEA pulping process is expressed as follow:

Pulp Screened Yield = +51.2283 + 0.303333A + 0.544619B – 0.950972C – 0.300143AB + 0.355AC + 0.526095BC-0.780833A²-0.378333B²-1.79653C² ……..…5

According to the monomial coefficient value of regression model Equation (5), X_1 = A = 0.303333 (Cooking Time), X_2 = B = 0.544619 (Liquor Concentration) and X_3 = C = -0.950972 (Liquor/Biomass Ratio), and the order of priority among the main effect of impact factors is Liquor-Concentration (X_2)>Cooking-Time (X_1)> Liquor/Biomass Ratio(X_3).

Diagnostics of the Linear Regression (Quadratic) Model

In statistics, the actual value is the value that is obtained by observation or by measuring the available data. It is also called the observed value. The predicted value is the value of the variable predicted based on the regression analysis. The difference between the actual value or observed value and the predicted value is called the residual in regression analysis. Each actual value has a predicted value and hence each data point has one residual. However, to evaluate this quadratic model, we regress predicted vs. actual (observed) values or vice versa and compare slope and intercept parameters against the 1:1 line. The residuals are represented graphically by means of a residual plot as shown in figure 3.29. 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. Here in figure 3.30, the residual plots are spread around the horizontal axis, indicating the appropriateness of the linear regression (quadratic) model. The Residuals vs. Predicted plot is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph). The graph of interaction of the three factors reveal that at 2% Polysulfide (O.D. wt. biomass), increase in Anthraquinone and Surfactant beyond 2.5% (O.D. wt. biomass), lead to corresponding decreased pulp screened yield.

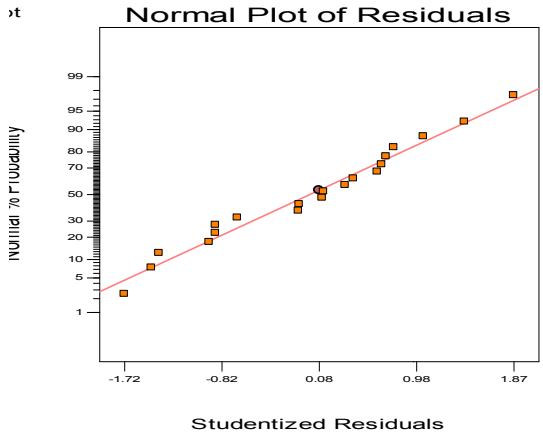

Figure 1. Normal probability plot of the studentized residuals to check for normality of residuals

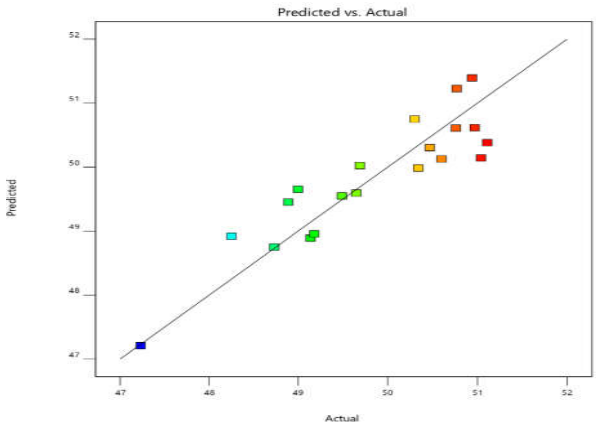

Figure 2. Plot of Predicted vs Actual Values

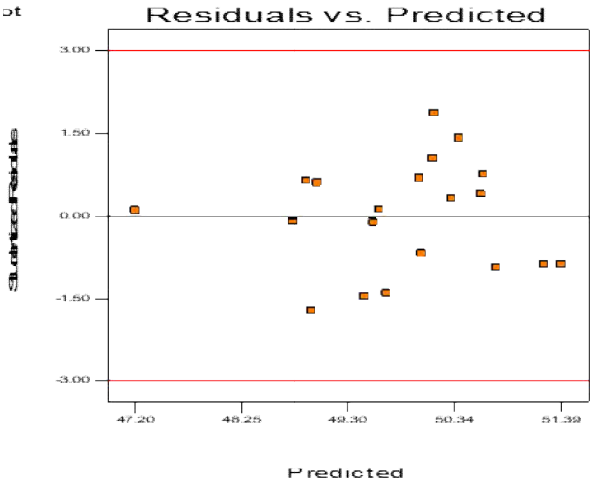

Figure 3. Studentized residuals versus predicted values to checkfor constant error

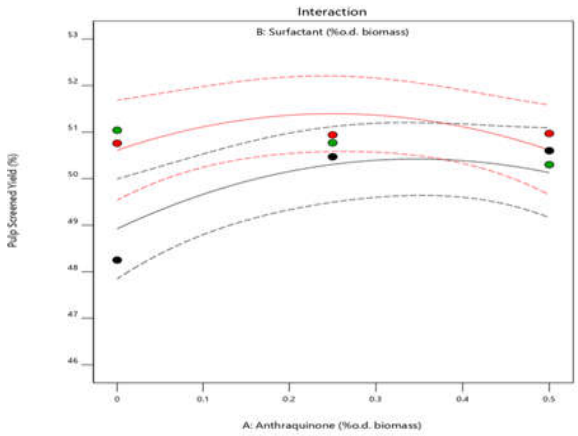

Figure 4. Describes the interaction of the three (3) factors in relation to pulp screened yield

The red dotted lines indicate points above and below design points, while the red curve between the dotted-line is the line of interaction between the two factors (AQ and Surf.). The interaction graph revealed that 2.5% AQ and Surfactant (O.D. wt. biomass) is a point of negative deviation in Pulp Screened Yield. It is also clear from the graph that the main interacting factors are anthraquinone and surfactant. However, the report summary of the diagnostics case statistics of the cooking operation and the interaction between the cooking additives is presented in Table 3.

Model Graphs

The contour model graph, figure 5 presents nine (9) design points. Eight (8) axial design points and one (1) central design point. The central design point is the point of optimum design of best combination of additives for the pulping operation and based on the interaction of the independent factors, the central design point indicates 0.25 % O.D. wt. anthraquinone and 0.25% O.D. wt. surfactant at 2% O.D. wt. polysulfide as the point of maximum yield for the pulping operation.

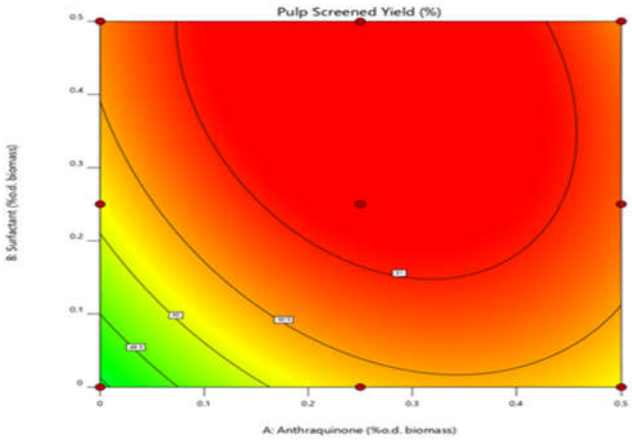

Figure 5. Contour Model Graph showing the Design Points of the Effect of the Interaction of the Factors (Independent variables) on Pulp Screened Yield

Curve fitting, also known as regression analysis, is used to find the "best fit" line or curve for a series of data points. There are six (6) design points around the 3D surface model graph described by Figure 6 which presents two (2) sets of design points. Five (5) design points above predicted value represented by red dots and one (1) design point below predicted value represented by lavender dots. The curve fitting on the 3D surface model graph examined the relationship between three predictors (independent variables i.e. anthraquinone, surfactant and polysulfide) and a response variable (dependent variable i.e. pulp screened yield), with the goal of defining a "best fit" model of the relationship. The red dotted lines are lines indicating on each factor the points of maximum yield. These are the design points of the optimum parameters of the independent variables furnishing the best pulping conditions as 90minutes cooking time, 75% liquor concentration and 6/1 liquor biomass ratio.

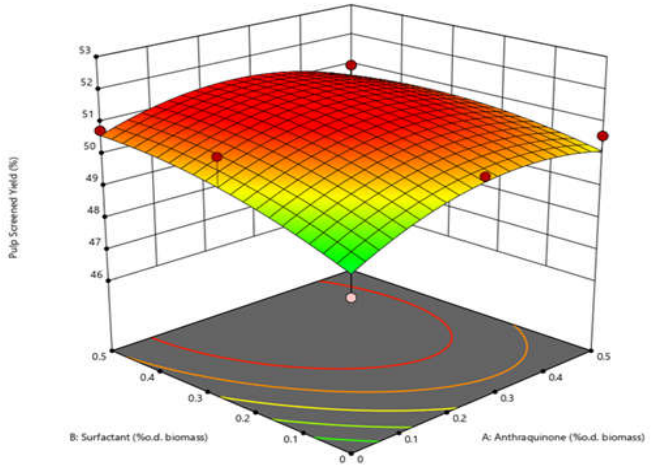

Figure 6. 3D Graph for the response surface Model

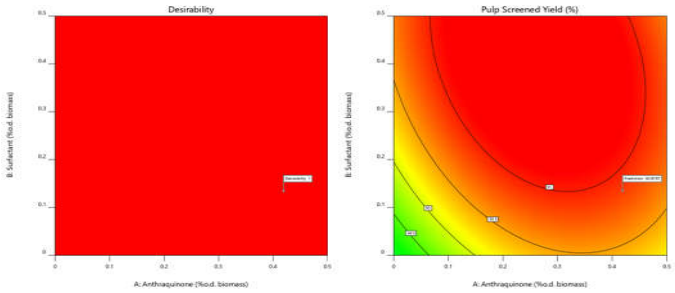

Figure 7. Optimization Contour Graph confirming Numerical Solution

The plot critical level is the confidence level at which the contour plots of the two data sets meet at a single point. This is the minimum confidence level at which the contour lines of the two different data sets overlap. At any confidence level below this minimum confidence level, the contour lines of the two data sets will not overlap and there will be a statistically significant difference between the two populations at that level. The overlap contour graph furnished X_1= 0.291 for anthraquinone and X_2= 0.413 for surfactant. We can then conclude that there is a statistically significant difference between the data sets at the 95% confidence level.

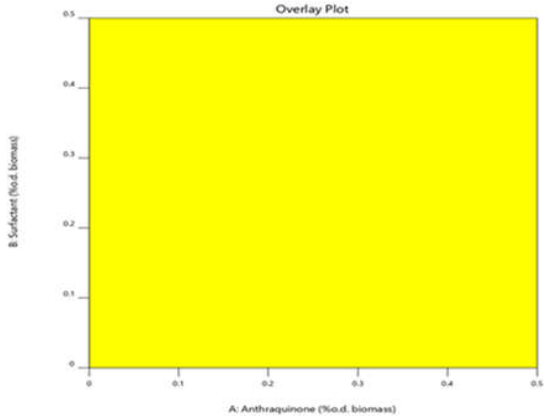

Figure 8. Overlay Contour Plot of Graphical Optimization solution for the AQ and Surf interaction

Conclusion

The results show that there is an impact of anthraquinone, surfactant and polysulfide over the screened yield and there is also an interaction between anthraquinone and surfactant. Based on the results obtained, the use of 0.25% of anthraquinone, 0.25% surfactant and 2% polysulfide led to the best results in terms of screened yield for the overall MEA pulping operations. But further investigation using series of statistical analysis presents: Anthraquinone = 0.291% o.d. wt. biomass; Surfactant = 0.413% o.d. wt. biomass and Polysulfide = 1.460 % o.d. wt. biomass with a response (Pulp Screened Yield) of 51.437. With the use of pulping additives like anthraquinone, surfactants, polysulfide and their conjunct use to enhance efficient delignification, MEA-pulping of EFB require less chemical consumption with higher pulp yield than the soda process without environmental damage. This process recorded an increase in the pulp production and lower cooking period was utilized to obtain the same pulp quality and quantity, making the implementation of this process possible in factories situated in the vicinity of agricultural areas, since it may be adapted for low productions and may be applied to any raw wood or non-wood material.

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