RESPONSE SURFACE METHODOLOGY TO OPTIMIZE THE YIELD OF ALKYD RESIN FROM JATROPHA *(JATROPHA CURCAS)* AND SESAME *(SESAMUM INDICUM)* SEED OILS

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ABSTRACT

Utilizing the response surface methodology (RSM) of the Box Behken model to optimize the alkyd resin yield factors from low-cost feedstocks such as sesame (*sesamum indicum*) and jatropha (*jatropha curcas*) seed oils were investigated. The experimentally chosen input factor ranges of oil:glycerol (0.3–1), phythalic anhydride: glycerol (1–3), and catalyst (0.5–1.5 wt. % for optimization were used. For each of these distinct alkyd resins, optimal yield, viscosity, and specific gravity quality data were collected. The alkyd resin outcomes from the two sets of combination variable tests were utilized to validate the expected technique. The optimization solution utilizing $CaCO_3$ catalysts and a combination of other process parameters assessed, as well as the related desirability functions, was discovered using analysis of variance (ANOVA) results for refined sesame alkyd resin (RSAR) and refined jatropha alkyd resin (RSAR) (RJAR). The optimization input variables for RSAR yield, used a $CaCO_3$ concentration of 1.5 wt. % at molar ratios of oil:glycerol (1.0:1.0) and phythalic anhydride:glycerol (3.0:1.0), while the RJAR used a similar catalyst concentration of 1.5 wt. % at molar ratios of oil:glycerol (1.0:1.0) and phythalic anhydride:glycerol (2.8:1.0). Under these conditions, the anticipated and experimental biodiesel yields for RSAR were 48.26 % and 47.29 %, and 62.07 % and 61.61 % for RJAR, respectively which shows less than 0.5 % variations. The effects of calcium carbonate catalyst dosages on the yield, viscosity, and specific gravity of alkyd resin generated from the RSAR and RJAR were major characteristics that considerably influenced the yield, while the specific gravity and viscosity only varied moderately. The regression model provided the multivariate analysis coefficients (R^2) as a variation of the mean, implying that the models were desirable.

KEYWORDS: Pptimization, Alkyd resin, Sesame, Jatropha, Seed oils,

1.0 INTRODUCTION

Naturally, there are several benefits to using renewable resources, including the availability of feed, their environmental friendliness, and their low cost [1]. The abundant agricultural and woodland resources in Nigeria produce a variety of oil-bearing items sowing plants [2-4]. Alkyds serve as binders, which makes them crucial basic components for producing a range of surface coatings, according to Aigbodion, *et al.* [5,6]. Alkyd chemists are looking for alternative, but more affordable, sources of surface-coating vegetable oils due to the rising cost of conventional vegetable oils used in coatings [7]. The manufacture and characterization of castor oil-modified alkyd resin for surface coatings were examined by Ikhuoria, *et al.* [8].

A combination of soybean oil, linseed oil, and partially and fully epoxidized vernonic oil was used by Muturi-Nwangi, et al. [9] to synthesize alkyd resins. Gogte and Sarwadekar [4] demonstrated that alkyd resin made from fractionated rice bran oil and castor oil was of very high quality. The outcome shown that rice bran oil enabled the use of maleic acid without

running the risk of the manufactured resins gelling. Igwe and Ogbobe [10] investigated the production of alkyd resin utilizing oils from rubber seed and melon seed through the alcoholysis-polyesterization process Shaker *et al* [11] developed oil-based alkyd resins made from jojoba seeds. The response surface methodology (RSM), which is based on computer simulations or experimental observations [13–15], was also developed by Box et al. [12]. Response surface techniques were utilized in this work to provide the most accurate examination of the influences on the yields of alkyd resin from jatropha and sesame seed oils.

2.0 MATERIALS & METHODS

2.1 THE GATHERING, EXTRACTION, AND REFINING OF SEEDS.

The sesame and jatropha seeds were gathered in Ilorin, Kwara State, Nigeria, from farms and marketplaces. For n-hexane extraction, a 40g of freeze-dried raw crushed sample was put in a beaker with 200 mL of n-hexane and stirred at 300 rpm for 20 hours at 45 °C. The extracted hexane solution was then evaporated at 400°C in a rotating vacuum evaporator and filtered with 125 mm grade filter paper. In the refining process, degumming, alkaline, and bleaching treatments were essential procedures for the elimination of impurities for successful trans-esterification [16–18].

2.2 ALKY RESIN PREPARATION IN TWO STAGES: ALCOHOLYSIS AND ESTERIFICATION

Stage of alcoholysis: The reactor was charged with 50 grams of each oil and 2 grams of the catalyst CaCO3. Then, the mixture was heated to about 120 °C. To cause the trans-esterification of triglyceride into a mixture of mono- and diglyceride oils, 20g of glycerol was added at 120 °C and heated to 230–250 °C with vigorous agitation for 30 minutes. When a sample of the combined substance became soluble in 1 to 3 liters of anhydrous methanol and produced a clear solution, alcoholysis was complete. The temperature of the reaction was lowered to 140°C to ensure a smooth transition to the esterification phase.

Stage of esterification: The temperature was decreased to 150 °C after 30 minutes, and 25g of phthalic anhydride was added before xylene. Before the temperature is raised to 245 oC with stirring, the esterification water is periodically withdrawn. Water and the unreacted acid were removed from the bulk by heating it to temperatures exceeding 250 oC and stirring constantly. The acid number and viscosity were measured at 30-minute intervals during the 5-hour reaction process.

2.3 OPTIMIZATION OF ALKYD RESINS BASED ON SEED OIL: The process optimization is required to produce high-quality goods with reduced drying periods, acceptable color, cheap production costs, and other desirable characteristics. Additionally, it is always considered to minimize the product's cost by reducing reaction time and temperature. The procedure was optimized using the MRS optimization method to generate a tailored response [20].

2.5 OPTIMIZING YIELDS THROUGH EXPERIMENTATION: RSM was used to establish the design of experiments (DoE) with a design input to measure the outputs or reaction. The glycerol/oil molar ratio (M1), catalyst (C), temperature (T), and glycerol/phthalic molar ratio are the DoE input variables employed (M_2). Box and Behnken (19) adopted the three components and three levels of a Box-Behnken Design (BBD). The glycerol/phthalic molar ratio (1-3), reaction NaOH catalyst (0.5-1.5 wt. %), reaction temperature (200-260 ° C), and glycerol/oil molar ratio are the chosen experimental parameters and their ranges for optimization (0.3-1). The projected measurable outputs are represented by the variable ranges in Table 1 as indicated.

Table 1: Levels of experimental design with independent variables.

Inputs	Notation	Levels		
		-1	0	+1
Phthalic/Glycerol	Phyt/Gly	1	2	3
Catalyst	Cat	0.5	1	1.5
Oil/Glycerol	Oil/Glyc	0.3	0.65	1

2.0 RESULTS AND DISCUSSION

3.1 ALKYD RESIN YIELDS ARE OPTIMIZED USING THE RESPONSE SURFACE METHODOLOGY.

To test the response of outputs, a design matrix (inputs) must be established; a Box-Behnkem design (BBD) with three variables and three levels was utilized. The design of experiments (DoE) was created using the inputs listed below: The following three ratios: oil-to-glycerol (oil/gly), phthalic-to-glycerol (phy/gly), and catalyst-to-glycerol (phy/gly) (cat.) Based on the results of the trials, the factor ranges covered the intervals that were frequently employed in the literatures: catalyst (0.5-1.5 wt. percent), Oil/Glyc (0.3-1), Phyt/Gly (1-3), and catalyst (0.5-1.5 wt.%)

3.1.1 REFİNED ALKYD RESİN MADE FROM JATROPHA

In this instance, 17 experiments were required to convert the whole set of options and select the best method for producing alkyd resin.The design matrix shows the total number of experiments as well as the values corresponding to each combination of variables (Table 2).

Table 2: Experimental design matrix for various input variables

	Factor 1	Factor 2	Factor3	Response	
Run	A:Oil/Glyc	B:Phyt/Gly	C:Cat g	Yield %	
				Actual	Predicted
1	1	2	1.5	55.8	56.64
2	0.65	2	1	22.4	22.40
3	0.65	2	1	22.4	22.40
4	0.3	1	1	5.15	4.94
5	0.65	2	1	22.4	22.40
6	0.65	3	0.5	43.2	42.42
7	0.3	2	0.5	14.65	13.81
8	0.65	2	1	22.4	22.40
9	0.65	3	1.5	46.6	45.55
10	1	3	1	58.7	58.91
11	0.65	1	1.5	30.48	31.26
12	0.65	1	0.5	25.69	26.74
13	1	1	1	50.55	48.93
14	0.3	2	1.5	18.37	17.80
15	0.3	3	1	23.29	24.91
16	0.65	2	1	22.4	22.40
17	1	2	0.5	52.4	52.97

Analysis of variance

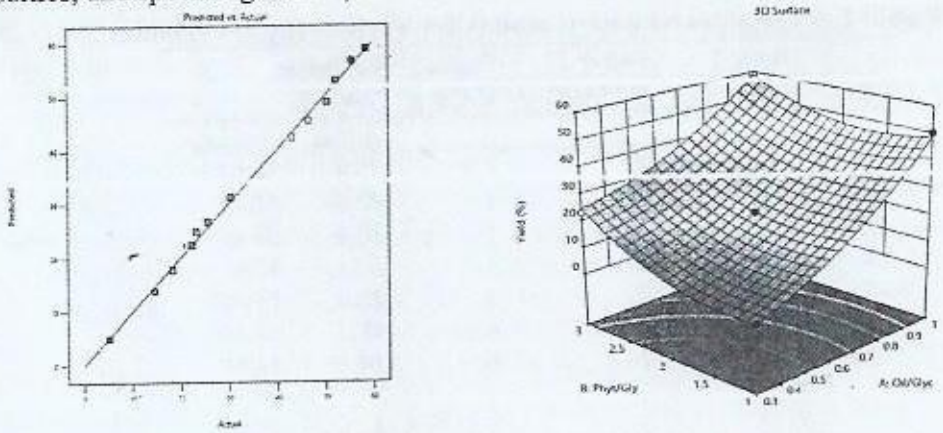
The second order polynomial functions that were acquired to model yield are shown in these equations. Yield is calculated as follows: +31.47181 + 12.94745 oil/glyc - 13.59679 phyt/gly - 54.38536 cat - 7.13571 oil/glyc*phyt*gly - 0.457143 oil/glyc*cat - 0.695000 phyt/gly*cat +44.22449 oil/glyc2 + 6.60500 phyt/gly + 29.95000 cat. (1)

Table 3 demonstrates the method used to determine the projected response using the regression equation. It is obvious that all of the data points are grouped together in the direction of the y=x line.

Table 3: Anova Table for the quadratic "yield" model

Source	Sum of Squares	Df	Mean Square	F-value	p-value (prob > F)	
Model	4150.88	9	461.21	297.84	< 0.0001	significant
A-Oil/Glyc	3041.61	1	3041.61	1964.20	< 0.0001	
B-Phyt/Gly	448.80	1	448.80	289.82	< 0.0001	
C-Cat	29.30	1	29.30	18.92	0.0034	
AB	24.95	1	24.95	16.11	0.0051	
AC	0.0256	1	0.0256	0.0165	0.9013	
BC	0.4830	1	0.4830	0.3119	0.5939	
A^2	123.58	1	123.58	79.80	< 0.0001	
B^2	183.69	1	183.69	118.62	< 0.0001	
C^2	236.05	1	236.05	152.44	< 0.0001	
Residual	10.84	7	1.55			
Lack of Fit	10.84	3	3.61			
Pure Error	0.0000	4	0.0000			
Cor Total	4161.72	16				

The scatter diagrams demonstrate agreement between the expected and observed yields, viscosities, and specific gravities, as shown in Table 2 and Figure 1.



(a) (b)

Figure 1: Scatter diagram of (a) yield and (b) corresponding 3D surfaces

Table 4: Optimization solution found according to RJAR optimization scenario

Number	Oil/Glyc	Phyt/Gly	Cat	Yield	Desirability	
1	1.000	2.621	1.500	62.066	0.932	Selected
2	1.000	2.628	1.500	62.162	0.932	
3	1.000	2.618	1.500	62.025	0.932	
4	1.000	2.642	1.500	62.345	0.932	
5	1.000	2.602	1.500	61.824	0.932	

The desirability functions for three distinct criteria using different input parameters (oil/glyc, phyt/glyc, and $CaCO_3$ catalyst) and the combination of procedures that were assessed are shown in Tables 2 and 3. The optimization solutions found for the alkyd resin optimization scenario are shown in Table 4. The results of the analysis of variance (ANOVA) utilizing the

average input variables catalyst (1.5 g), oil/glyc (1.0), and phyt/gly (1.0), the optimization solution yield was 62.066 % with the chosen overall attractiveness of 0.932. (2.621).

3.1.2 ALKYD RESIN DERIVED FROM REFINED SESAME

To convert the full range of alternatives and choose the optimum alkyd resin production procedure in this case, 17 experiments were also necessary. The design matrix displays the number of experiments and the pertinent values for the variable combination (Table 5).

Table 5: Experimental design matrix for various input variables

Std	Run	Factor 1 A:Oil/Glyc	Factor 2 B:Phyt/Gly	Factor3 C:Cat g	Response Yield %	
					Actual	Predicted
8	1	1	2	1.5	50.55	51.96
14	2	0.65	2	1	38.55	38.55
13	3	0.65	2	1	38.55	38.55
1	4	0.3	1	1	4.35	9.34
15	5	0.65	2	1	38.55	38.55
10	6	0.65	3	0.5	24.9	30.60
5	7	0.3	2	0.5	16.21	14.80
17	8	0.65	2	1	38.55	38.55
12	9	0.65	3	1.5	25.29	28.88
4	10	1	3	1	59.285	54.29
11	11	0.65	1	1.5	28.52	22.82
9	12	0.65	1	0.5	24.68	21.09
2	13	1	1	1	45.25	49.55
7	14	0.3	2	1.5	9.415	10.12
3	15	0.3	3	1	24.47	20.17
16	16	0.65	2	1	38.55	38.55
6	17	1	2	0.5	47.995	47.29

Analysis of variance

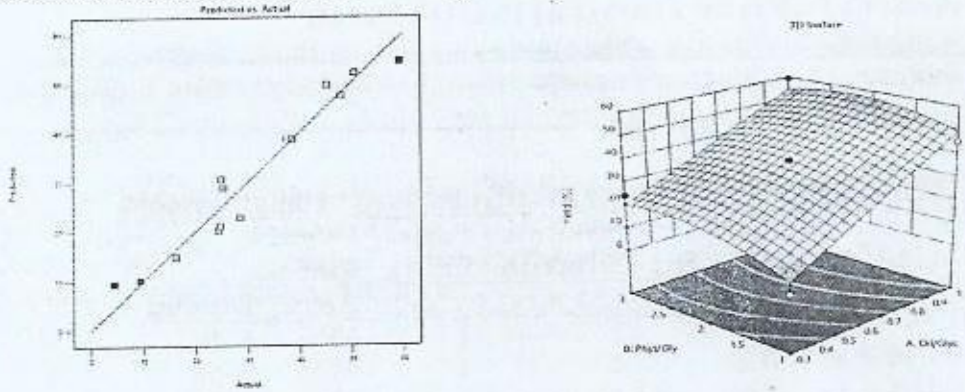
These equations display the computed second order polynomial functions for modeling yield. Yield is equal to: -54.99454 + 48.50587 Oil/Glyc + 29.25580 Phyt/Gly + 54.76036 Cat - 4.34643 Oil/Glyc*Phyt/Gly + 13.35714 Oil/Glyc*Cat - 1.72500 Phyt/Gly*Cat - 0.066327 $Oil/Glyc^2$ - 5.20312 $Phyt/Gly^2$ - 29.99750Cat^2

(2)

Table 6: ANOVA Table for the quadratic "yield" model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	3288.15	9	365.35	14.01	0.0011	significant
A-Oil/Glyc	2761.55	1	2761.55	105.86	< 0.0001	
B-Phyt/Gly	121.25	1	121.25	4.65	0.0680	
C-Cat	0.0000	1	0.0000	4.792E-07	0.9995	
AB	9.26	1	9.26	0.3549	0.5701	
AC	21.86	1	21.86	0.8378	0.3905	
BC	2.98	1	2.98	0.1141	0.7455	
A^2	0.0003	1	0.0003	0.0000	0.9975	
B^2	113.99	1	113.99	4.37	0.0749	
C^2	236.80	1	236.80	9.08	0.0196	
Residual	182.60	7	26.09			
Lack of Fit	182.60	3	60.87			
Pure Error	0.0000	4	0.0000			
Cor Total	3470.75	16				

In Table 6 and Figure 2, the projected yields, viscosity, and specific gravity are in line with the actual values, according to scatter diagrams.



(a) (b)

Figure 2: Scatter diagram: (a) yield and (b) with the corresponding 3D surface

Table 7: Optimization result based on the RSAR optimization scenario.

Number	Oil/Glyc	Phyt/Gly	Cat	Yield	Desirability	
1	1.000	3.000	1.500	48.264	0.909	Selected
2	1.000	3.000	1.500	48.265	0.909	
3	1.000	3.000	1.500	48.265	0.909	
4	1.000	3.000	1.495	48.388	0.908	
5	1.000	2.978	1.500	48.455	0.908	

The desirability functions for three different criteria are shown in Tables 5 and 6 using a variety of input parameters. The optimization solutions found for the alkyd resin optimization scenario are shown in Table 7. According to the results of the analysis of variance (ANOVA), glycerol, phythalic acid, and the catalyst doses were all important in the production of alkyd resin. Phyt/glyc (3.00), oil/glyc (1.000), and catalyst (1.5 wt%) were average input variables used in the optimization solution, which had an alkyd resin yield of 48.264 % and an overall desirability of 0.909

Table 8: Optimization result based on the RSAR optimization scenario.

Sample	Oil/Glyc	Phyt/Gly	Cat	Yield	Desirability	
RSAR	1.000	3.000	1.5	48.264	0.909	Selected
RJAR	1.000	2.621	1.5	62.066	0.932	Selected

Tables 8 show the optimization results using $CaCO_3$ catalysts and a variety of additional process variables that were studied, as well as the associated desirability functions. The RJAR used a similar $CaCO_3$ concentration of 1.5 wt. %, at molar ratios of Oil/Glyc (1.0/1.0) and Phyt/Glyc (2.621:1.0), to obtain 62.066 percent yield with a desirability of 0.932. The RSAR optimization used $CaCO_3$ concentration of 1.5 wt. % at molar ratios of Oil/Glyc (1.0:1.0) and Phyt/Glyc (3.0). During the alkyd resin optimization for the two methods, average input variables including catalyst concentration of 1.5 weight percent, molar ratio of Oil/Glyc (1.0:1.0), and Phyt/Glyc (2.621:3.0), were noted.

3.2. THE FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS OF ALKYD RESINS

The existence of a hydroxyl group in the alkyd resin is confirmed by an absorption band at 3461.74 cm^{-1} in the RSAR FT-IR spectra (Figures 3 and 4). While a signal at 1720.32 cm^{-1} confirmed the presence of a C=O carbonyl functional group of a carbonyl compound, an absorption band at 1448.02 cm^{-1} indicated the presence of sp^3 (CH_3 bend) hybridized carbon of aliphatic compounds, and a signal at 2920 cm^{-1} indicated the presence of a C-H stretching vibration of an sp^3 carbon or aliphatic compounds. The appearance of a peak at 1071.24 cm^{-1} indicates the presence of C-O stretching vibration.

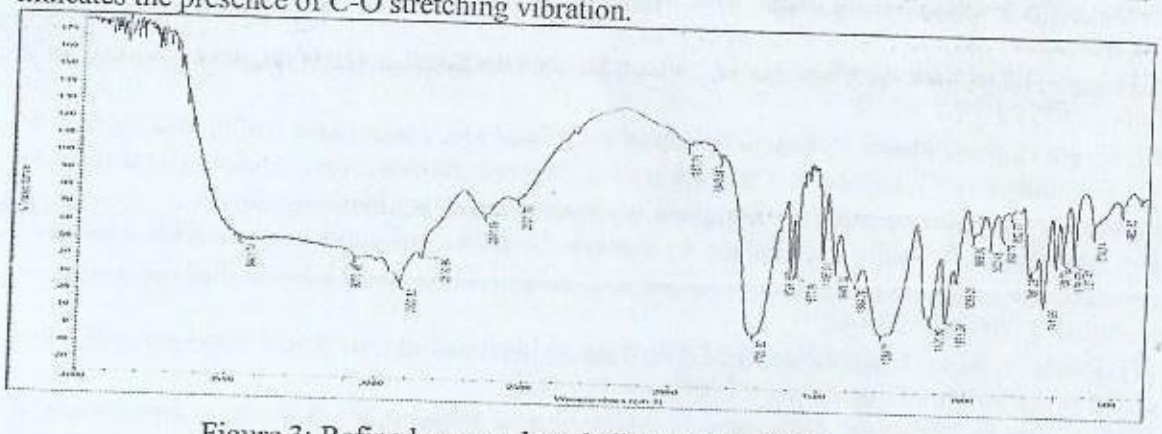


Figure 3: Refined sesame-based alkyd resin's FTIR spectrum.

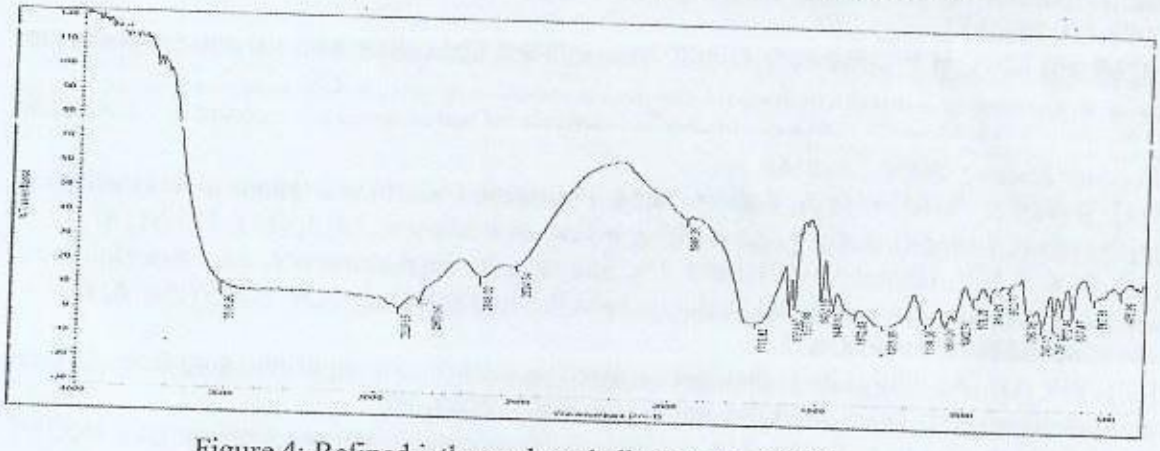


Figure 4: Refined jathropa-based alkyd resin's FTIR spectrum.

Figure 4 and Table 11 indicate that the Fourier Transform Infrared (FTIR) spectra of RJAR contain an absorption band at 3518.86 cm^{-1}, which denotes the presence of a hydroxyl group in the alkyd resin. While the signal at 1710.82 cm^{-1} confirmed the presence of the C=O carbonyl functional group of the carbonyl compound and the absorption band at 1448.02 cm^{-1} showed the presence of sp^3 (CH_3 bend) hybridized carbon of aliphatic compounds, the signal at 2926.65 cm^{-1} indicated the presence of C-H stretching vibration of an sp^3 carbon or aliphatic compounds C-O stretching vibration is present, as evidenced by the growth of a peak at 1134.24 cm^{-1}.

5. CONCLUSION

The findings of the ANOVA showed that although the non-edible seeds used to make the oil were different seeds, the molar ratio of the oil to glycerol and the glycerol to phthalic, as well

as the catalyst, speed, and time, were significant determinants of the alkyd resin output. The highest alkyd resin yielded 62.066 % for RJAR and 48.263 % for RJAR under these circumstances, respectively.

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