OPTIMIZING THE ESTERIFICATION PROCESS OF RSO MODIFIED WATER BORNE ALKYD RESIN USING RESPONSE SURFACE METHODOLOGY (RSM)

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ABSTRACT

The optimization of esterification process of self-emulsifying method of rubber seed oil (RSO) modified water borne alkyd resin was investigated. Response surface methodology (RSM) analysis using design matrix of FFA linked with CCRD in coded notation for RSO modified water borne alkyd resin synthesis was used to optimize important process parameters comprising the reaction temperature, catalyst ratio, reaction time, oil ratio, viscosity, molecular weight of the resin coupled with their interaction on the oil sample. The optimum conditions (reaction temperature of 260^0*C ,reaction time of 180 mins, oil ratio of 0.43, catalyst ratio 0.1, stirring rate of 500rpm) were determined by the results of statistical screening analysis under which the experiment was performed. The results obtained revealed that the maximum responses of 89.66% fractional conversion, viscosity of 293.197Cp,average molecular weight of RSO water borne alkyd MW(av) of 5481 were determined based on economic consideration. Hence, the experimental value of 0.89 was in accordance with the predicted modal value of 0.89.*

Keywords: Rubber Seed Oil, Water Borne RSO Alkyd, Process Optimization, Self-Emulsification, Response Surface Methodology.

1.0 INTRODUCTION

The global surface coating industry is a multi-billion dollar industry which provides a vehicle for motivation of this paper to synthesized rubber seed oil modified water borne alkyds that not only uses local raw materials but also zero volatile organic compounds (VOC) that have serious negative effects on both environment and human health. There is need to utilise less expensive and non-edible product oil in the synthesis of the water borne RSO resin in order to meet up with the competitive environment of coating industries. One of such oil product which can be utilized to yield a desirable result both in terms of cost, non-edible, renewable and biodegradable is rubber seed oil (RSO). Alkyd resins are the most versatile of coating binders and they are used extensively in all major categories of coatings: architectural, industrial, and special purposes (Wang, 2000). The popularity of alkyds as vehicles in coating are due to their film hardness, durability, gloss, and gloss retention, abrasion resistance and other characteristics imparted on them through modification of the drying oil (Majumdar et al, 1998).

The replacement of solvent based binders by water soluble counterparts has steadily gained popularity for obvious reasons of increasing awareness about the health concerns, adverse effect of the organic solvent emissions on the environment and safety measures of water. It must be mentioned that solvent based alkyds when compared to the water borne coatings zero volatile organic compounds (VOC), odours, decrease flammability, improve safety and offer easy friendly interactions. Human beings who are subjected to VOC for extended periods are under the risk of contracting Organo Psycho Syndrome (OPS) and psycho-neurological disease (PND) Vander et al, 1999. These obvious reasons are some factors that attracted a great deal of attention of the research paper towards searching for alternative raw materials in vegetable oils and fats industry in particular non-edible and non-drying oils. In addition, the coatings of conventional alkyd resin with any oil content or acid value are solvent based usually diluted in an organic solvent such as toluene, xylene and different oil cuts or a mixture of these solvents (Yousefi et al, 2011).

Rubber seed oil (RSO) has shown strong potentials in the manufacture of alkyd resin for use as binders in surface coatings , polymer processing and diesel fuel substitute and extender.. It has also been used as partial substitute to mineral oil as carrier for copper fungicide in the management of abnormal leaf fall disease of rubber in an attempt to reduce cost without compromising on the efficacy of diseases control. Rubber seed oil (RSO) has been found to have potential applications in many areas amongst which are in the production of biodiesel as fuel for compression engines (Ramadhas, 2005), foaming agent in latex foam, in the synthesis of alkyd resin used in paints and coatings . It is semi-drying and consists of 17-22% saturated fatty acids and 17-82% unsaturated fatty acids and is comparable to drying oils commonly used in surface coating. However, research has shown that RSO to be rich source of oil that is comparable in quality to dry oils commonly used in surface coating. Oil modified alkyd resin remains the work – horse of many coating system, especially in the automotive industry. This is due to some of its short comings such as poor adhesion, poor abrasion resistance and low viscosity. Several physical and chemical modification of the oils to enhance their initial quality have been evolved over the years. Example of such modification techniques include: acrylation, catalytic and thermocatalytic, polymerization, interesterification, phosphorrylation and expoxidation.

The physico-chemical properties of these major contributing variables to the process response would be achieved through design of experiment (DOE) and analysis of variance (ANOVA) while the control and optimization tasks would be accomplished using response surface methodology (RSM).Response surface methodology (RSM) refers to a collection of statistical and mathematical techniques that are used to create, improve and optimize a given process (Myers, 2002). The most used method is response surface methodology (RSM) adopted by a great degree of researchers (Acherjee et al, 2012, Muhamad et al, 2013, Meng, 2011, Noshadi, 2012). The models were generated by the quadratic polynomial approximation function. The design phase used several techniques to determine the inputs that correlate with the experiments such as central composite design and Taguchi (Cuevas et al, 2009). The more complex statistical and mathematical models were later used for experimental design using partial or full factorial (Box et al, 2005). The main goal of RSM is the development of a mathematical model of a given system based on experimental results. When non-linear interactions are foreseen, experiments at higher levels become a necessity to achieve good modeling, considering a minimum of five points is required to obtain a response curve (Myers et al, 2002). In this study, central composite rotable design was used to optimize the process conditions for the self -emulsification of rubber seed oil modified water borne alkyd resin because it guarantees advantage of minimized number of distinct investigations. The design phase used several techniques to determine the inputs that correlate with the experiments such as central composite design and Taguchi (Cuevas et al, 2009). Statistical method was applied to the experimental results to generate the mathematical model. The most used method is response surface methodology (RSM) adopted by a great degree of researchers (Acherjee et al, 2012, Muhamad et al, 2013, Ikezue, 1998, Meng, 2011, Noshadi, 2012).

2.0 EXPERIMENTAL

2.1 *Materials.*

The rubber seed oil (RSO), distilled water, methanol were obtained from H .B.M Onitsha in Anambra State Nigeria. Ammonia 25%, phthalic anhydride with assay 99.7%, maleic anhydride with assay 99.0%, glycerol with assay 99.7%, xylene and calcium oxide were obtained from B.D.H chemical ltd, Poole England. Triethylamine, hydrochloric acid, hydrogentetraoxosulphate (vi) acid, hydrogen-peroxide, glacial acetic acid were also purchased from Merck chemicals Germany. All the reagents were commercial grade and were used without further purification.

2.2. *Methods of chemical modification of RSO*

Rubber seed oil as non-drying was chemical modified (desaturation) to be very suitable for rubber oil modified water borne alkyd resin through series of process reactions such as:
epoxidation, hydroxylation of the epoxidized oil and dehydration of hydroxylated oil (Odetoye, 2012).

2.2.1 *Epoxidation of the crude RSO .*

150cm^3 of crude RSO was poured in a round bottomed flask, while 1.5cm^3 of 30% H_2O_2, 7.5cm ^{3} glacial acetic acid and 1.5cm^3 conc. H_2SO_4 were added in succession to the oil and stirred continuously using a stir hot plate without applying heat. Per acetic acid was generated from acetic acid and hydrogen peroxide in the presence of strong H_2SO_4. The reaction was maintained at room temperature and left overnight. The resulting layer was separated from the aqueous layer and washed with 15cm^3 of saturated solution of sodium bicarbonate. The oily layer obtained was subsequently washed seven times with distilled water after which it was dried at 80^{o}C for 45mins by using a vacuum pump.

2.2.2 H*ydroxylation of the epoxidized oil*

The obtained epoxidized oil (135 cm^3) was then heated to 98-100°C. 1.5cm^3 of dilute H_2SO_4 was added and the mixture was stirred intermittently for about 90mins. The oily layer was separated from the aqueous layer using a separating funnel after which it was dried at 80^{o}C for 45mins using a vacuum pump.

2.2.3 *Dehydration of hydroxylated oil.*

120cm^3 of the hydroxylated oil was poured into a three-necked reaction flask. Four drops of concentrated H_2SO_4 were added as catalyst for the dehydration process to speed up faster. The reaction time was maintained for 60mins at 260^{o}C and an inert atmosphere was ensured by nitrogen gas. The water generated from the distillate was collected through a dean-stark apparatus. 108cm^3 of dehydrated obtained at the end of the reaction for the samples products.

2.2.4 *Preparation of RSO alkyd resins*

Table 2 shows the formulation of three different RSO water borne alkyds prepared with dehydrated rubber seed oil, glycerol, phthalic anhydride, maleic anhydride using calcium oxide as catalyst . The reactions were carried out in a two-litre three necked round bottom flask titled with a motorized stirrer, a dean-stark trap titled with water-cooled condenser and nitrogen in let tube at a temperature of 230-250^{0}C. Xylene (cooking solvent) was also employed as the azeotropic solvent. Two stages were involved.

Stage- 1 (Alcoholysis): At this stage, the measured quantity of dehydrated rubber seed oil was poured into the flask and heated to about 120^{0}C to remove moisture. The heating was achieved with a heating mantle. Then, the measured quantity of glycerol was added and the temperature was raised to 230^{0}C. After 30 minutes, a small quantity of the aliquot was taken to check for its solubility in methanol. Alcoholysis was completed when the solubility test in methanol was positive . The reaction mixtures were cooled to about 140^{0}C.

Stage -2 (Esterification process): At this stage, the measured quantity of phthalic anhydride, maleic anhydride and xylene was added into the flask and heated with a heating mantle. The temperature was gradually raised to about 230^{0}C and maintained at a range of about 230-250^{0}C for about 3 hours. Aliquots were withdrawn from the reaction mixture at time intervals of 40minutes for accurate periodic determination of acid value drop. The reaction was then discontinued as soon as the acid value of the mixture attained the value of about 10mg K0H/g.

Table 1: Formulation for the Compositions of (RSO) Modified Water Soluble Alkyd Resins.

Water Soluble Resin type	Dehydrated Oil length (%)	Glycerol (g)	Calcium oxide (g)	P A (g)	M A (g)
Alkyd RS-A	37	20	0.2	40	15
Alkyd RM-B	53	20	0.2	40	15
Alkyd RL-C	71	20	0.2	40	15

Table 2: Formulation Composition of Ingredients for the Solubility of Different Solvents for Synthesis of Water Soluble Alkyd Resin.

Ingredients	Required amounts %
Amount of alkyd resin neutralization	65-80
Neutralizing aqueous solution(water soluble solvents) conc(M)	0.1-0.2
Co-solvents	21-27
Distilled water	24-26

2.3 DESIGN OF EXPERIMENT:

Independence factors and corresponding levels used for the control and optimization of esterification process are shown below.

Table 3: Important Process Parameters and their Levels.

Factors	Range and levels				
	-α	-1	0	1	+α
Temp(^{o}C) A	230	260	290	320	350
Time(min) B	60	90	120	150	180
Oil ratio C	0.1	0.2	0.3	0.4	0.5
Catayst D	0.1	015	0.20	0.25	0.3
Stirring(rpm)E	500	550	600	650	700

3.0 RESULTS AND DISCUSSION.

3.1 *Synthesis of water borne RSO Alkyd Resins*

The technique of self-emulsifying process was used to synthesize water borne RSO alkyds. In the process of the poly-condensation reaction, the concentration of the three different alkyd resins modified RSO prepared were further incorporated with some water soluble monomers in the various alkyd resins mixture. The mixture of each type of resins was subsequently cooled to 120^0c .The modified alkyds in the presence of the monomers (aqueous base solution –ammonia, triethanolamine, potassium hydroxide and triethylamine). The choice of these organic bases was selected based on its ability to ensure a good neutralization of carboxylic groups and on its influence on film aspect as well as drying time. Ammonia and triethylamine showed that the neutralization process on the agents was satisfactorily realized .It was discovered that ammonia gives the most reduced drying time among other bases (Andresi, 2015). From the experimental result obtained, it was discovered that triethanolamine and ammonia showed sticky appearance on the film while with ammonia no difference on the colour appearance of water borne RSO alkyd. Once the resin is neutralized, must be solubilized in the co-solvents. . The co-solvent used were BG and BUOH also confirmed very soluble with the resin together with water as shown in the formulation table above.

This process was carried out by progressively adding water- solution containing neutralized aqueous solution. The ensuing binder is also emulsified in water after neutralization step without the use of volatile organic solvents to confirm the progress in emulsification process. Self-emulsifying properties of the water borne RSO alkyds was based on the result of the dissociation of the acidic carboxylic groups (-COOH) coming from the aqueous solutions .The self-emulsifying method is also applicable on fast development on industrial scale which is a unique characteristics over other approaches: incorporating ionizable hydrophilic groups that will ensure electrostatic stabilization. The use of mini-emulsion approach which is hindered by technical difficulty to ensure the mini-emulsification of the alkyds in the monomers but method of ultrasonication cannot be applied on an industrial scale. The resulting mixture of each RSO alkyd resins emulsion was further homogenized by mechanical stirring for 25 minutes to ensure a complete emulsification process when phase reverse emulsification occurs. The product obtained was subjected to mehmet oven at temperature of 100^0c to ensure zero organic solvent thereby water borne RSO alkyd resin products were passed through gas chromatograph to ensure efficient water borne RSO alkyd products which records 22.7% VOC. The water borne RSO alkyds synthesized by this mechanism improves the rate of homogeneity and compatibility between the two phases and useful in modern trend of industrial production for water borne RSO alkyds over other approaches.

3.2 The five level fractional factorial array linked with central composite rotable design (CCRD) was used to account for the overall process variability and minimize the total number of experimental runs. The design was made of five levels the usual $\pm s$, $\pm \alpha s\ and\ 0s\ notations\ to$ designate the factorial, axial and central points respectively. This amounts to a total number of 30 experimental training comprising 16 runs at 24-full factorial levels, eight at the axial points and 6runs at the centre points plus system of aliases /E/ as shown in the table 3. From the preliminary experiments, the range and levels used in the experiments were selected also from table 2. The experimental design matrix for the synthesized water borne RSO alkyd resin by CCRD was illustrated in table 3 and corresponding experiments were appropriately performed. For the purpose of the statistical computations, the five independent variables were denoted as × 1 ,× 2 , - - - ×4 and ×5 respectively.

Tables 4: Design Matrix of FFA for the Synthesis of Water Soluble RSO Alkyd Resin linked with CCRD in coded notation.

Run	Design space	Independent variables					Responses		
		A	B	C	D	|E|	Y_1	Y_2	Y_3
1	Factorial	-1	-1	1	1	1	62.1	216.5	2438
2	Factorial	1	1	1	1	1	90.1	228.4	4890
3	Factorial	1	1	1	-1	-1	80.5	290.6	4995

4	Factorial	-1	-1	1	-1	-1	38.8	162.4	693.9
5	Factorial	1	-1	-1	1	1	77.5	249.9	3620
6	Factorial	1	-1	1	-1	1	68.8	239.3	3088
7	Factorial	1	-1	1	1	-1	70.8	273.7	4436
8	Factorial	-1	1	-1	-1	-1	60.2	215.9	2533
9	Factorial	1	1	-1	1	-1	78.1	279.8	4292
10	Factorial	1	1	-1	-1	1	77.4	260.9	3790
11	Factorial	-1	1	1	-1	1	76.2	259.6	3886
12	Factorial	-1	-1	-1	-1	1	30.1	140.3	500
13	Factorial	-1	-1	-1	1	-1	30.4	140.9	500
14	Factorial	-1	1	-1	1	1	63.3	230.5	2993
15	Factorial	1	-1	-1	-1	-1	42.3	177.8	1270
16	Factorial	-1	1	1	1	-1	78.6	275.8	4640
17	Axial	-α	0	0	0	0	70.1	240.7	3336
18	Axial	A	0	0	0	0	50.6	180.8	1200
19	Axial	0	-α	0	0	0	82.4	273.6	4445
20	Axial	0	α	0	0	0	42.4	166.6	839
21	Axial	0	0	-α	0	0	65.5	228.4	2921
22	Axial	0	0	A	0	0	54.7	199.5	1947
23	Axial	0	0	0	-α	0	80.7	269.8	4294
24	Axial	0	0	0	A	0	60.1	214.4	2111
25	Axial	0	0	0	0	-α	77.7	258.9	3850
26	Axial	0	0	0	0	A	74.9	250.2	3830
27	Center	0	0	0	0	0	74.4	255.1	3980
28	Center	0	0	0	0	0	74.1	255.4	3980
29	Center	0	0	0	0	0	74.6	255.7	3986
30	Center	0	0	0	0	0	74.5	255.9	3988

Where: A = Temperature; B = Time; C = Oil Ratio; D = Catalyst Conc.; |E| = Stirring rate aliased to highest order interaction effect of the other process variables; Y_1 = Conversion; Y_2 = Viscosity; Y_3 = Molecular weight average.

The results obtained were analyzed by using the coefficients of determination R-squared (R^2), response plots and analysis of variance (ANOVA) .Moreover, since there is a curvature in the response surface, then a higher degree polynomial equation should be used to fit the experimental data and evaluate the relevant model. The approximating function with 2 variables is called a second –order model, it could be given as:

$$\gamma = \beta 0 + \beta 1 \times 1 + \beta 2 \times 2 + \times \beta 11 \times 1^2 + \beta 22 \times 2^2 + \Sigma \beta iJ \times 1 + \Sigma \beta ij \times 2 + \quad \Sigma \qquad (1)$$

Where γ predicted represents the predicted response i.e., the gradual decrease of iodine value as the reaction progress, $\beta 1$ the ith linear coefficient of the input factors $\times 1$, $\beta 11$ the ith quadratic coefficient of the input factors $\times 1$, βiJ the different interaction coefficients between input factors ×i and ×ij such that i = 1,5, j = 1,5 and 1± j and Σ, the error of the model. The equation actually expresses the relationship between the predicted responses and the independent variables in the coded values according to the tables 3 and 4 respectively.

3.3 *Optimization of Esterification Process*

The optimization of esterification study on the synthesis of RSO modified water borne alkyd resin design matrix as shown in table 3.The experimental results obtained from the above table showed that 30 experimental runs and fractional conversion for the RSO modified water borne alkyd resin designated with Y was estimated in terms of the measured reduction in the iodine value over the reaction time. The response Y recorded for the different runs confirmed that the process factors have noticeable effects.

3.4. *Statistical Screening Analysis of RSO modified Water soluble Alkyd Resin*

To examine the effect of the identified system parameters which include; temperature, reaction time, oil ratio, catalyst concentration and stirring rate A, B, C, D and E respectively on the molecular properties (conversion, viscosity and $MW_{(av)}$) of RSO water soluble modified alkyd resin for the proposed method, a surrogate model of the system was derived from multi-regression analysis. The global matrix equation thus:

$$\text{Polycarboxylic acid} + \text{Polyalcohols} + \text{Fatty acids} \rightarrow \text{alkyd resin} + H_20 \qquad (2)$$

was fitted to the data provided by the combined array given in Table 2 to obtain the predictive models equations (3, 4, 5). The resulting models, therefore, were adjusted in terms of only the significant system variables to obtain the predictive model equations (6, 7, 8). The coefficients of determination R–squared (R^2) values of 0.9236, 0.9455 and 0.9639 obtained for Y_1, Y_2 and Y_3 based esterification processes, respectively, show that more than 92% of the total variability arising from the system can be explained by the empirical models of equations (3,4, 5), which are specific cases of the general predictive equation derived for individual investigations based on statistical screening analysis from the multivariate regression analysis implemented on design expert.

$$\gamma = \beta 0 + \beta 1 \times 1 + \beta 2 \times 2 + \times \beta 11 \times 1^2 + \beta 22 \times 2^2 + \Sigma \beta iJ \times 1 + \Sigma \beta ij \times 2 + \quad \Sigma \qquad (3)$$

$$Y_1 = 73.83 + 7.70A + 10.98B + 5.34C + 4.91D + 2.98E - 3.14AB - 3.12A - 2.91BE - 3.40A^2 - 2.88B^2 - 3.46C^2 - 0.56D^2 - 1.12E^2$$

(4)

$$Y_2 = 253.15 + 21.98A + 29.33B + 15.75C + 12.88D + 4.02E - 9.68AB - 7.73BD - 5.50BC - 6.35BE - 1.11ABC - 2.12BCD - 9.37A^2 - 7.03B^2 - 8.57C^2 - 20.10D^2 - 0.19E^2 \tag{5}$$

$$Y_3 = 3935.67 + 686.21A + 945.25B + 479.87C + 475.74D + 78.55E - 272.94AB + 71.94AE - 219AD - 68.50ACE - 56.70ACDE - 239.44BD - 227.94BE - 173.18CE - 106.19DE - 350.49A^2 - 256.93B^2 - 308.99C^2 - 116.78D^2 - 310E^2 \tag{6}$$

$$Y_1 = 73.83 + 7.70A + 10.98B + 5.34C + 4.91D + 2.98E - 3.14AB - 2.91BE - 3.40A^2 - 2.88B^2 - 3.46C^2 \tag{7}$$

$$Y_2 = 253.15 + 21.98A + 29.33B + 15.75C + 12.88D + 4.02E - 9.68AB - .73BD - 6.35BE - 9.37A^2 - 7.03B^2 - 8.57C^2 \tag{8}$$

$$Y_3 = 3935.67 + 686.21A + 945.25B + 479.87C + 475.74D + 78.55E - 272.94AB + 71.94AE - 239.44BD - 227.94BE - 173.18CE - 106.19DE - 350.49A^2 - 256.93B^2 - 308.99C^2 - 116.78D^2 \tag{9}$$

Where $Y_1, Y_2\ and\ Y_3$ are the predicted values of the dependent variables investigated. The coefficients $A, B, C, D\ and\ E$ are main linear effects of the independent process variables temperature, time, oil ratio, catalyst concentration and stirring rate, respectively, in coded units as shown in Table 3.1. $AB, AD, AE, BD, BE, CE\ and\ DE$ represent the linear interaction effects between temperature/time, temperature/catalyst concentration, temperature/stirring rate, time/catalyst concentration, oil ratio/stirring rate and catalyst concentration, respectively. $A^2, B^2, C^2\ and\ D^2$ are the quadratic effects of the respective process variables. The estimated coefficient terms reveal that quadratic interactions of system variables show negative effects while the main linear and first order interaction effects are positive. Higher order interaction terms are not significant in the model. The "Predicted R-Squared" of 0.7621, 0.7856 and 0.7414 are in reasonable agreement with the respective "Adjusted R-Squared" of 0.8833, 0.9122 and 0.9195; and the Model F-values of 22.96, 28.40 and 21.70 further indicate that the models are significant. There is only a 0.01% probability that the "Model F-Values" this large could occur due to noise. P Values of less than 0.05 indicate model terms are significant. "Adequacy Precision" measures the signal to noise ratio (SN). A ratio greater than 4 is desirable. SN values 16.384, 18.318 and 14.430 indicate adequate signal-to-noise ratios. These models can be used to navigate the design space. The ANOVA results derived from the predictive models show that the main linear effects due to individual control factors coded $A, B, C, D\ and\ E$ respectively are significant variables indicated with the observed p-values < 0.05 in the numerical analysis. This is equally true with the linear interaction effects between temperature and time (AB), time and stirring rate (BE) and (for $Y_2$and Y_3analysis) time and catalyst concentration (BD). The quadratic effects of temperature, time and molar ratio denoted by $A^2, B^2\ and\ C^2$ respectively are significant for the molecular properties $(Y_1\ and\ Y_2)$. In Y_3, however, the quadratic effect due to catalyst concentration D^2 in addition to $A^2, B^2\ and\ C^2$ emerge significant in the models.

3.5. *Process Analysis and Control Using RSM.*

The well-known RSM was considered appropriate due to its flexibility in navigating the design space .The responses obtained from the esterification process for the synthesis of RSO modified water borne alkyd resins were presented in Table 3. The analyses and optimization exercises were completed accordingly using the design expert 9.1 trial application while the numerical and graphical solutions were presented in triplicate for easy comparison as response surface contour diagrams. They were analyzed collectively based on the various solutions obtained at possible reaction conditions from the model predictive equations 3, 4, 5.These equations were solved for the various interaction effects on RSO water borne alkyd resin conversion considering at any instance the interactions between two factors only, assuming the other variables are set at their mean coded value of zero. The interaction effects on the process response between temperature $(A)$and time (B) in their natural units associated with the three responses are presented in Figure 1.

Table 5: ANOVA for the Response Quadratic Model

Source	F-Value			P-Value		
	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3

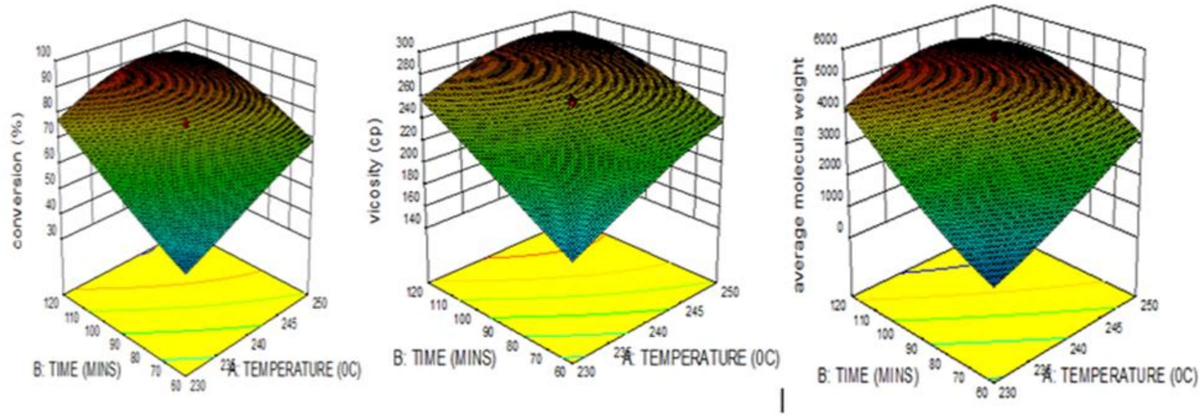
Model	22.96	28.40	21.70	<0.0001	<0.0001	<0.0001
A-Temp.(Celcius)	48.03	71.86	73.05	<0.0001	<0.0001	<0.0001
B -Time(Minutes)	97.73	127.94	138.62	<0.0001	<0.0001	<0.0001
C -Mole Ratio	23.12	36.89	35.72	<0.0001	0.0001	0.0001
D-Catalyst Conc.(w/w)	19.52	24.67	35.11	<0.0003	0.0001	<0.0001
E-Stirring rate (rpm) AB						
BE	7.17	2.40	0.96	0.0149	0.1387	0.3458
BD	5.32	9.28	7.71	0.0326	0.0069	0.0157
A^2	4.58	4.00	5.37	0.0455	0.0608	0.0374
B^2	-	5.93	5.93	0.0206	0.0255	0.0300
C^2	10.90	15.23	21.78	0.0037	0.0010	0.0004
D^2	7.86	8.58	11.70	0.0113	0.0090	0.0046
	11.31	12.74	16.93	0.0033	0.0022	0.0012
	-	-	2.42	-	-	0.1439
Conversion (Y_1)	Std. Dev. 5.44 R-Square 0.9236 Mean 66.06 Adj R-Square 0.8833 C.V. % 8.24 Pred R-Squared 0.7621 PRESS 1751.62 Adeq Precision 16.384					
Viscosity (Y_2)	Std. Dev. 12.71 R-Square 0.9455 Mean 233.17 Adj R-Squared 0.9122 C.V. % 5.45 Pred R-Square 0.7856 PRESS 11433.56 Adeq Precision 18.318					
Molecular weight average (Y_3)	Std. Dev. 393.32 R-Squared 0.9523 Mean 3109.10 Adj R-Squared 0.9308 C.V. % 12.65 Pred R-Squared 0.8679					

	PRESS 1.44E+007 Adeq Precision 14.430

DF: Model = 9, Residual = 20, Total = 29

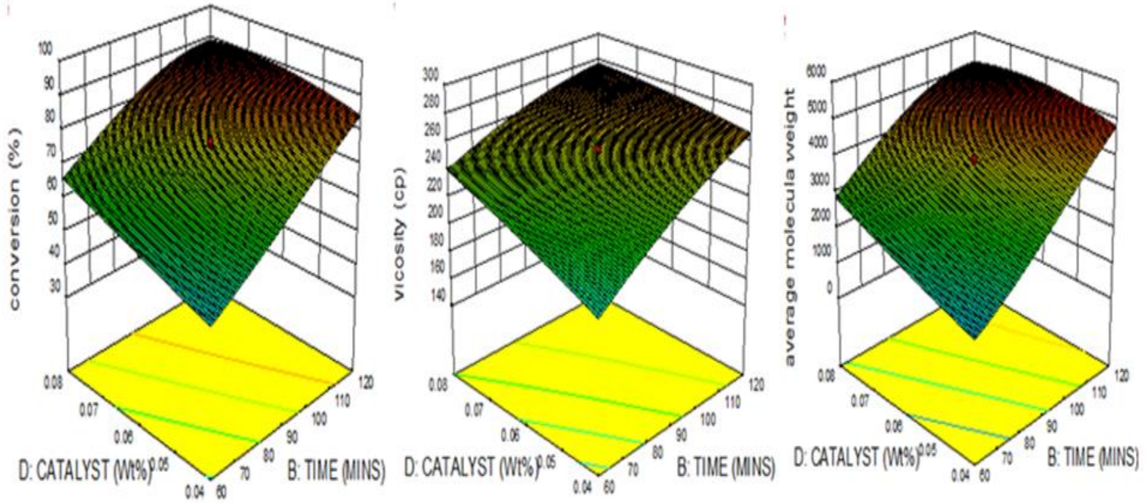
As expected for a typical batch process, the fractional conversion, viscosity and $MW_{(av)}$ of the RSO modified water borne resins generally increases readily with reaction time, approaching 75%, 250 Cp and 3800 units at 116 minutes, respectively, even at low level temperature setting of about 230^0C indicating high rate of conversion of COOH and OH to COOR in sufficient monoglyceride oil. Towards the end of the reactions, the responses indicate lower conversion because COOH may have been used up. This observations conform to a large extent with the results of literature (Okon and Ibanga, 2014). Moreover, significant curvature was observed with the responses as temperature is adjusted through its range especially in the $y1$ axis. The responses increase as temperature setting shift from 220^0C to 240^0C and begin to show depreciating values at higher isotherms above 260^0C still on the same $y1$ axis. This might be due to the reversible nature of the esterification process and possible existence of critical factor settings that guarantees optimum conversion of a desired resin with desired polymerization properties under atmospheric condition and necessary trade-off (adequate economic value) that may justify the efforts of experimental design and the optimization studies. The responses, however, seem to increase uniformly at higher isotherm for viscosity and $MW_{(av)}$ up to and even beyond gelation point. This equally, may be due to astronomical increase of viscosity with temperature and time; even in the absence of noticeable reaction. From Figure 1B, the quadratic effect of temperature is identified with smooth curves on the reference surface contour, however, the quadratic effect of time appears unidentified, but the increase in reaction time at a low temperature of about 230^0C gave rise to an increased viscosity to 250 Cp. Increase in reaction time to 120mins at constant temperature of about 260^0C rapidly increase the viscosity nearer to its optimum value. In Figure 1C, the quadratic effect of temperature and time was observed with smooth wave like curves on the reference surface contour and good $MW_{(av)}$ greater than 3600 can be seen at a moderate temperature and time between (90 to 100) translating to a tremendous energy savings.

The response for the interaction of time and catalyst concentration is presented in Figure 2. From Figure 2A, increasing reaction time at a very low catalyst weight of about 0.04% will increase conversion reasonably and even the maximum conversion may be obtained by simply maintaining the weight at 0.04% and increasing the time from 90 to 95 mins. Obviously, it will be a waste using larger weight of catalyst. The interaction effect of catalyst and time is not evident as little variation in the changes of the responses when catalyst concentration was reviewed upward to 0.08% was observed. However, from Figure 2D, increase in $MW_{(av)}$ is noticeable. An interesting observation was recorded in Figure 2A and 2D where the responses show intrinsic similarities in the two orthogonal axes. It can therefore be concluded that it is advisable and more economical to carry out the poly-condensation process with a low catalyst weight of 0.04wt % and then increasing the reaction time to about 90 to 100 minutes.



(A) (B) (C)

Figure 1. Interacting effect of temperature and time on conversion, viscosity and Molecular weight average ($MW_{(av)}$) on three-dimensional response surface plot.



(A) (B) (D)

Figure 2: Interaction effect of catalyst and time on conversion, viscosity and molecular weight average on three-dimensional response surface plot.

3.6 *Optimization process*

Optimization is a process of finding the set of conditions needed to achieve the best process results from a given system. The optimization process involves the synthesis of water borne RSO alkyd resin that will provide some obvious advantages like short drying time a critical issue associated with non-drying oil, high resistance in alkali and other chemical media, reduced material cost, improve film properties , improved colour (appearance), viscosity, and molecular weight. Other advantages from the chosen optimization process is through reduced reaction time and temperature which in effect minimizes the overall cost of the synthesis of resin (Uzoh et al, 2013).Significant economic benefit may be derived by optimizing the molecular properties which relate to the end-use properties of the RSO modified water borne alkyd resin during synthesis. These molecular properties are required to lie within some desired optimal in the parameter design space. Considering the current study, the characterization-control-optimization algorithm base on a 2^{5-1} FFA adequately guaranteed the detailed process analysis and optimization of the RSO modified alkyd resin molecular properties.

The processing of high quality alkyd resin from water soluble RSO and high commercial importance necessarily require optimization of the polycondensation process with particular in focus on the molecular properties as the output responses. This was achieved in the present study through formulation of a global optimization criteria based on RSM upon which the necessary trade-off of system variables were implemented. Such systematic compromise was particularly important in the process described above since the system responses show peak values at non-unique locations within the variable design space. The entire exercise was aided by the numerical optimization tool function of the Design Expert statistical software (trial version 9.1) used for the experimental analysis. Equations (3, 4, 5) were solved for the best solution(s) such that the responses Y_1, Y_2 and Y_3 were maximized. No unique solution was attainable. The various solutions obtained were assessed based on their contribution to maximum responses and other necessary economic consideration. From ten best optimal solutions obtained as shown in table 3.2, a credible optimum solution of 89.66% fractional conversion, viscosity of 293.197 Cp and $MW_{(av)}$ of 5481 predicted at temperature of 260^0C, time of 180 min, oil ratio of 0.43, catalyst ratio of 0.1 and stirring rate of 500 rpm at 0.99 desirability were selected based on economic consideration and necessary trade-off. A repeated correspondence investigation performed following the predicted optimal conditions record 89.1% fractional conversion, viscosity of 293.4 Cp and $MW_{(av)}$ of 5450 for the studied RSO modified water borne alkyd resin. This figure represents 0.65% average maximum prediction error.

Effort to compare these solutions overtly with previous works found in literature did not provide much desired result. This is because optimization of esterification process on the synthesis of water borne alkyd resins via statistical screening analysis, especially for the molecular properties have not received adequate research attention deserved of them. However, it has been shown that a lot of similarities exist between the results of current research and a previous work (Uzoh et al, 2013, 2015) where more than 97% of the esterification process of monoglyceride of palm oil, coconut oil and phthalic anhydride was completed within the first 150mins of reaction at temperature maintained between 230-241^0C. On the other hand, the overall review observations contained in this study were apparently different from those reported in literatures (Govannilton et al, 2011; Freedman et al, 1984; Encinar et al, 2002). This may be attributed to the inherent high activation energy associated with the equilibrium of reaction between polybasic acid, polyhydric alcohols and the glyceride oils to form alkyd resin.

Table 3.2. Optimum Values of Process Variable for Maximum Responses

Independent variables					Responses			
A	B	C	D	E	Y_1	Y_2	Y_3	Desirability
269.171	180	0.44	0.1	500.037	89.825	293.792	5525.195	0.998

266.511	179.999	0.452	0.1	500.022	89.812	293.974	5532.362	0.998
269.291	179.835	0.433	0.1	500.005	89.784	293.590	5514.740	0.998
263.911	179.999	0.433	0.1	500.005	89.779	293.727	5513.742	0.998
271.096	179.959	0.465	0.1	500.078	89.758	294.057	5550.196	0.998
265.745	179.999	0.471	0.099	500.097	89.707	294.072	5543.746	0.998
265.878	180	0.417	0.099	504.448	89.671	293.049	5462.226	0.998
260.708	**179.999**	**0.43**	**0.1**	**500.047**	**89.66**	**293.197**	**5481.260**	**0.998**
272.413	177.577	0.439	0.1	500	89.606	293.405	5517.305	0.997
262.339	179.765	0.405	0.1	500.001	89.596	292.597	5450.142	0.997

Where: A = Temperature; B = Time; C = Oil Ratio; D = Catalyst Conc.; E = Stirring rate; Y_1 = Conversion; Y_2 = Viscosity; Y_3 = Molecular weight average (MW_{av}).

CONCLUSION

The results obtained from this study revealed that oil modified water borne alkyd resin stand out clearly as the main work-horse for global surface coating industry. The application of response surface methodology (RSM) based on central composite notable design (CCRD) used for the analysis and optimization of the self-emulsifying methods of RSO modified water borne alkyd resin showed and confirmed that optimum solutions of process parameters for maximum responses of 89.66% fractional conversion at reaction temperature 260^{0}C of time 180 mins, oil ratio of 0.43, catalyst ratio of 0.1, stirring rate of 500rpm. The design of experiments were employed in this study for optimization since it takes into account the interactive effects between the input parameters. Research has shown RSO to be rich source of oil that is comparable in quality to dry oils commonly used in surface coating .It can be concluded that RSO modified water borne alkyd resin offer greater potential applications in surface coating purposes.

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