

# Kinetic Model of The Polyesterification Reaction of The Investigative Study of The Optimum Unsaturated Fatty Acid Content For Auto- Oxidative Drying of Palm-Stearin-Based Alkyd Resin

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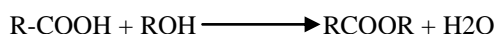
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**Abstract:** The kinetic study of the synthesis of an auto-oxidative drying modified palm stearin based alkyd resin was based on the polyesterification reaction process. The polyesterification process of the alkyd synthesis was studied using regression analysis of viscosity as a function of time applying integral method. The pendant chain of the Palm Kernel Stearin (PKS) was modified by blending it with measured ratio of rubber seed oil (RSO), followed by dehydration of the oil blend with the aim of increasing the degree of unsaturation in the oil chain. The modified dehydrated palm kernel stearin oil blend with ratio of 80:20, 75:25, 70:30 and 65:35 by wt./wt.% of PKS to RSO respectively labelled as Oil A, Oil B, Oil C and Oil D were used to synthesized Alkyd A, Alkyd B, Alkyd C and Alkyd D respectively using a two stage alcoholysis-poly-esterification method. The film properties of synthesized alkyds were determined as well as the drying schedule with the aim of getting optimum ratio of PKS to RSO which will yield auto-oxidative drying alkyds as regards to the total PKS content of the oil blend. Alkyd C gave the best result from the characterization and investigation study. The result of kinetic studies of the poly-esterification reaction of the synthesized alkyds shows that Alkyd A and B follows first order kinetics with rate constant of 0.0119/mins and 0.0136/mins whereas as Alkyd C and D follow second order kinetics with  $0.0026 \text{ (Pa S)}^{-1}/\text{min}$  and  $0.0026 \text{ (Pa S)}^{-1}/\text{min}$ , none follows third order kinetic.

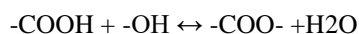
**Keywords:** Palm kernel stearin; auto-oxidative drying; alkyd resin; kinetic study; organic coating.

## 1. INTRODUCTION

Alkyd resins have been defined as the product of polycondensation reaction between a polyhydric alcohol modified with a monobasic acid or its anhydrides and drying oil with suitable catalyst at controlled temperature [1]. The basic reaction involves in the esterification of the alkyd resin.



The kinetic model of alkyd resin synthesis is based on the polyesterification reaction between the hydroxyl group of the monoglycerides and carboxylic group of the polybasic acid or its anhydrides. Thus, the poly esterification reaction during the synthesis of an alkyd resin can be experimentally followed by titrating for the unreacted carboxyl groups with a base, i.e., monitoring the acid value. Considering a simple esterification reaction below



Alkyd resins are used in the formulation of paints, varnishes, lacquers and other finishes. Alkyd resins have become an indispensable raw material due its extensive usage for decorative and protective purposes. They are of enormous importance in the building industry where they are used for interior and exterior architectural finishes [2]. Lately, the

use of edible oil in the synthesis of alkyd resin is increasing day by day and this poses a great danger in the availability of such oil in the food sector. The high costs, the environmental impact, and the decrease in fossil resources are the main reasons behind attracting a great deal of attention of the research community towards searching for alternative raw materials in different industrial fields. So, with the increase in world demand for oil and the challenges to expand the existing oil supply for human consumption and industrial utilization [3], there is need to utilize less expensive and non-edible product (oil) in the synthesis of the alkyd resin in order to meet up with the competitive environment of the coating industries.

One of such product which can be utilized in the synthesis of surface coating generally to yield a desirable result both in terms of cost, renewability, biodegradability and non-edibility is palm kernel stearin (PKS).

Oil Palm (*Elaeis guineensis*) is native to Africa and remains a source of the most abundant and widely used plant oils in the world, grown en mass in tropic countries. Palm oil and palm kernel oil are edible plant oil derived from fruit of the trees. It differ from its major competitors (soybean, sunflower seed and rape seed) in that it is obtained from perennial tree crop and drought impact are less severe in comparison to oil seed crops.

Palm stearin are more solid fractions of palm and palm kernel oils. It has not been commercially utilized and almost a non-useful product in most part of the world. The fatty acid composition of palm kernel stearin is approximately 60% saturated and 40% unsaturated fatty acid. The main unsaturated fatty acids compositions of palm kernel stearin are 33% oleic and 7% linoleic acid [4]. Therefore, palm kernel stearin are classified as saturated fatty acid due to its very low degree of unsaturation and alkyd resins, which are based on palm kernel stearin alone, cannot be air-dried [5]. In order to air dry, palm kernel stearin based alkyd resin, an unsaturated C=C bonds must be introduced into the main or pendent chains of the alkyd resin. In this current research, a new recipe was developed to increase the degree of unsaturation in the main chain of palm kernel stearin structure before using it in the synthesis of auto-oxidative drying alkyds. Measure ratios of Palm kernel stearin were blended with different measured ratios of rubber seed oil. The different blended oil ratios undergoes dehydration process at temperature of 150°C before it is used in the alkyd synthesis which involves the reduction of the triglycerides oil (palm kernel stearin + rubber seed oil) by the alcoholysis process to obtain modified palm kernel stearin mono glyceride at 230°C, followed by functional group modification with phthalic anhydrides via poly esterification at temperature range of 230°C to 250°C. The synthesized alkyds which has different oil content as regards to the Palm kernel stearin to rubber seed oil were each characterized to determine the physio-chemical and mechanical properties as well as the drying schedule and chemical resistance properties with the aim of getting the alkyds which gives desirable results as regards to auto oxidative drying bearing in mind the optimum (minimum) unsaturated fatty acid content (Rubber seed oil content) of the total mono glycerides oil content. The test of the kinetic order of reaction for the poly esterification reaction of the synthesized alkyds were also investigated using the integral method [6] adopting regression analysis to determine the rate constant and reaction order of each of the synthesized alkyd samples and implemented on the Microsoft excel spread sheet software program 2010.

#### ***Kinetic Modelling of the Polyesterification reaction***

The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups [17]. Thus, the poly esterification of alkyd resin esterification process can be experimentally followed by titrating for the unreacted carboxyl groups with a base, i.e., monitoring the acid value. Considering a simple esterification reaction below



The rate of polymerization, R, can then be expressed as the rate of disappearance of carboxyl groups as shown below.

$$R = - \frac{d[\text{COOH}]}{dt} = K[\text{COOH}][\text{OH}] \quad (2)$$

For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric (Fried, 2003), and "Equation 2" can be written as

$$R = - \frac{d[A]}{dt} = K[A]^2 \quad (3)$$

$$R = - \frac{d[A]}{[A]^2} = K dt \quad (4)$$

Where [A] is the concentration of –OH groups or –COOH groups

However, "Equations 2 and 3" show that synthesis of biopolymers follows second – order reaction, with K as the second order rate constant.

By integrating “Equation 4” with the boundary conditions;  $t=0$  and  $t=t$ , we have a second order rate constant.

$$- \int \frac{d[A]}{[A]^2} = \int K dt \tag{5}$$

$$1 / [A]_t = 1 / [A]_0 \tag{6}$$

Where:  $[A]_0$  is the initial concentration at  $t = 0$

$[A]_t$  is the concentration after time,  $t$ , of hydroxyl or carboxyl groups respectively.

## II. EXPERIMENTAL

### 2.1 Material

The palm kernel stearin was collected from the Upglobal Agro oil mill, Isiakpu village Nise, Anambra State. The refined rubber seed oil was purchased from the Rubber Research Institute of Nigeria, Iyanomon, Benin city and was used without further purification. The analytical grade phthalic anhydrides, glycerol, Calcium oxide, Sodium bisulphate (NaHSO<sub>4</sub>) and xylene were obtained from Eddy chemical shop in Onitsha and were used without further purification. The experimental equipment/ apparatus used in this research work were hired from the Spring board Laboratory research institute Awka Anambra state, Nigeria.

### 2.2 Instruments and Methods:

The fatty acid profile the oil were determined with a Thermo Finnigan Trace GC/Trace DSQ/A1300, (E.I Quadropole) equipped with a SGE-BPX5 MS fused silica capillary column (film thickness 0.25 $\mu$ m) for GC-MS detection, and an electron ionization system with ionization energy of 700eV was used. Carrier gas was helium at a flow rate of 10mL/min. injector and MS transfer line temperatures were set at 2200C and 2900C respectively. Viscosity was determined by Brookfield viscometer, RVT

Model (#Spindle 3, RPM 20). The physico-chemical properties of the oil were determined by standard methods (ASTM, 1973). The kinetic study was carried out using regression analysis and implemented using Micro soft excel program 2010

### PROCESS FLOW DIAGRAM FOR THE SYNTHESIS AND CHARACTERIZATION OF THE MODIFIED PALM STEARIN BASED

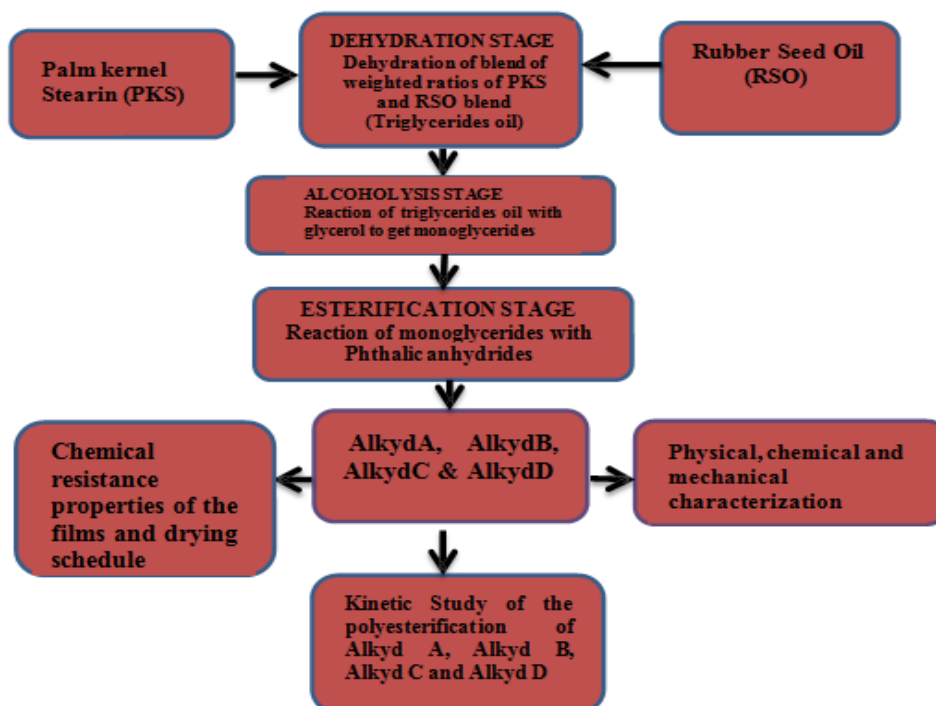


Figure 1. Process diagram for the modified palm kernel stearin based Alkyd resin synthesis and characterization.

### 2.3 Dehydration of Modified Palm Kernel Stearin:

The mixture of the palm kernel stearin-rubber seed oil undergoes dehydration process in order to get homogeneous mixture before it is used in the alkyd formulation.

80g of palm kernel stearin was blended with the 20g of rubber seed oil and labelled as oil A, The oil A was reacted with 1% weight NaHSO<sub>4</sub> catalyst in a round bottom flask fitted with a thimble and a condenser (soxhlet apparatus). The mixture was heated to a temperature of 150°C for 45mins with a mechanical stirrer which helps for the complete mixture of the two oils.

The same procedure was used for the dehydration of the palm kernel stearin – rubber seed oil mixture to get Oil B, Oil C and Oil D respectively but with different ratios of 75:25g, 70:30g, and 65:25g of palm kernel stearin to rubber seed oil respectively.

### 2.4 Alkyd Resin Synthesis

The types of oils used highly affect the properties of alkyds produced. Especially, the unsaturation contents of oils are of extreme importance because it determines the extent of drying.

#### 2.4.1 Selection of oil content:

In this study, the main objective is to improve the drying and physio-chemical properties of palm kernel stearin modified alkyd resin by introducing unsaturation to the pendent chain of the palm kernel stearin before using it for the alkyd resin synthesis. Oil A, Oil B, Oil C and Oil D were each used to produce different alkyds and the produced alkyds were characterized to know the oil content which gives the optimum result.

#### 2.4.2 Synthesis of alkyd from modified palm kernel stearin (oil A to D):

Four different medium oil length palm kernel stearin modified alkyd resin were synthesized with Oil A, Oil B, Oil C and Oil D respectively with the glycerol (50g), and phthalic anhydride (50g) using 3% wt. (0.03wt) calcium oxide catalyst and 5% wt xylene as the dehydrating agent and labelled as Alkyd A, Alkyd B, Alkyd C and Alkyd D accordingly.

In the preparation of the alkyd resin, two stages were involved. The first stage was alcoholysis stage and the second stage was esterification stage.

**Stage 1 (alcoholysis):** In this stage, monoglyceride was first synthesized by reacting the selected oil ( oil A, oil B, oil C or oil D) with 50g of glycerol in a round bottom flask fitted with a thimble and a condenser (soxhlet apparatus). Alcoholysis of the oil mixture was carried with 3% by weight of the oil, Calcium oxide catalyst.

In alcoholysis reaction, the selected oil together with the glycerol and the selected catalyst (Calcium oxide) were heated with agitation speed of (700rpm) at a temperature range of 230°C to 250°C. The completion of Alcoholysis was monitored by taking samples of the reaction mixture every 5 min. Each sample was mixed with anhydrous methanol in a 1:2 volume ratio until a clear solution was obtained which indicated the end of alcoholysis process. After the completion of the alcoholysis reaction which lasted for 50 minutes, the reaction mixture was cooled to the temperature of 150°C

**Stage 2 (esterification):** In this stage, 50g of phthalic anhydride and 10ml of xylene (azeotropic solvent) were added to the monoglyceride mixture, after which the temperature was increase from 150°C to the temperature range of 250°C. During this esterification stage, the reaction is continued at constant temperature and long chain molecules were formed which contain excess hydroxyl group. At this state, water was released and the mixed vapor generated was then cooled and collected and disposed properly. Xylene which is the dehydrating agent was suitably applied for this process considering its boiling point (140°C) and solubility in water. The reaction progress was monitored by periodic determination of the acid value by titration in accordance to ASTM D1980-87 (1998) with some modifications of the mixture at 30minutes interval until the acid value dropped below 10. The same procedure was used in the production of Alky A-D but with the associated oil A -D.

**TABLE I: Recipe used for the synthesis of four different medium oil length modified palm kernel stearin based alkyd resin**

Recipe	Alkyds			
	Alkyd A	Alkyd B	Alkyd C	Alkyd D
Palm kernel stearin (g)	80	75	70	65
Rubber seed Oil (g)	20	25	30	35
Glycerol (g)	50	50	50	50
Phthalic anhydrides (g)	50	50	50	50

**2.5 Evaluating the Coating properties of the Synthesized modified Palm Kernel Stearin base alkyds.**

**2.5.1 Characterization Test**

The physio-chemical properties (such as acid value, saponification value, specific gravity, iodine value and dynamic viscosity.) of the synthesized alkyds were determined using ASTM standard methods [7]

**2.5.2 Chemical Resistance Test**

The Chemical resistances of the four different medium oil length palm kernel stearin modified alkyl resins films after air drying the films for 48hours were determined in three media; distilled water, 0.1 moles of sodium hydroxide and 0.1 moles of Hydrochloric acid. After the time period, the weight loss was measured. The more the weight loss, the less the resins are resistant to the respective chemicals. An expression of the measurements such as No effect (not affected), whitening (not affected but change in color), Blistering (less affected) and Removal (affected) were used to indicate the chemical resistivity of the film with respect to their weight loses.

**2.5.3 Drying Test**

The prepared alkyd resin were thinned with xylene and applied as thin panels. The samples were checked frequently to trace the dryness or tackiness by using the finger tips and drying time monitored with the stop watch.

**2.5.4 Mechanical Test**

**2.5.4.1 Impact Resistance Test:** Impact test is used to establish the stone-chip resistance of coatings. For this test a Gardner Impact Test (model 5524) was used

**2.5.4.2 Adhesion Test:** This test was performed to measure the strength of the bonds formed between the coating material and the applied surface. Cross-cut test (ASTM D 3359) was used for the adhesion test.

**2.5.4.3 Pencil scratch hardness test:** This test was performed to measure the hardness of the alkyds films. Pencil scratch hardness tester (ASTM D 968) were used to carry out the test.

**2.6 TEST FOR THE KINETIC ORDER OF REACTION FOR THE SYNTHESIZED ALKYD RESINS.**

Regression analysis of viscosity as a function of time using integral method [6] was used to obtain first, second and third order kinetic model equations for the polyesterification reaction process during the synthesis of the alkyds.

First order kinetic model

$$R = -\frac{d[A]}{dt} = K[A]$$

Rearranging and integrating with boundary condition at t=0 and t= t

$$-Kt = \ln u - \ln u_0$$

$$\ln u = -Kt + \ln u_0 \tag{7}$$

Second order kinetic model.

$$R = -\frac{d[A]}{dt} = K[A]^2$$

Rearranging and integrating with boundary condition at t=0 and t=t

$$1/u = Kt + 1/u_0 \tag{8}$$

Third order kinetic model.

$$R = -\frac{d[A]}{dt} = K[A]^3$$

Rearranging and integrating with boundary condition at t=0 and t=t

$$-2Kt = 1/u_0^2 - 1/u^2$$

$$1/u^2 = 2Kt + 1/u_0^2$$

### III. RESULTS AND DISCUSSION

#### 3.1 The GC-MS result of Palm kernel stearin:

The GC-MS result and fatty acid profile (Interpretation of GC-MS result) of the Palm kernel stearin is shown in figure2. As expected, the fatty acid profile reveals that the Palm kernel stearin is predominated by saturated stearic acid (39.55%), myristic acid (6.59%), lauric acid (18.11%), magaric acid (11.58) and palmitic acid (6.15%), also the result shows that Palm Kernel Stearin contain unsaturated linoleic acid (6.17%) and palmitoleic acid (11.85%). The high saturated fatty acid in Palm kernel stearin from the result indicates that if palm stearin is used in the synthesis of alkyds, it will produce alkyds of slower drying rate but color retentive. Palm kernel stearin, therefore, if structurally modified, may give alkyd resin with better performance characteristics.

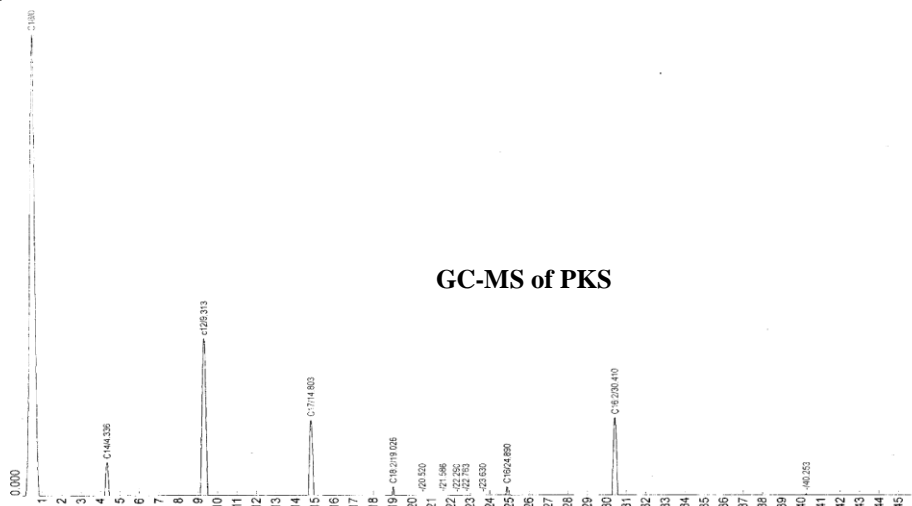
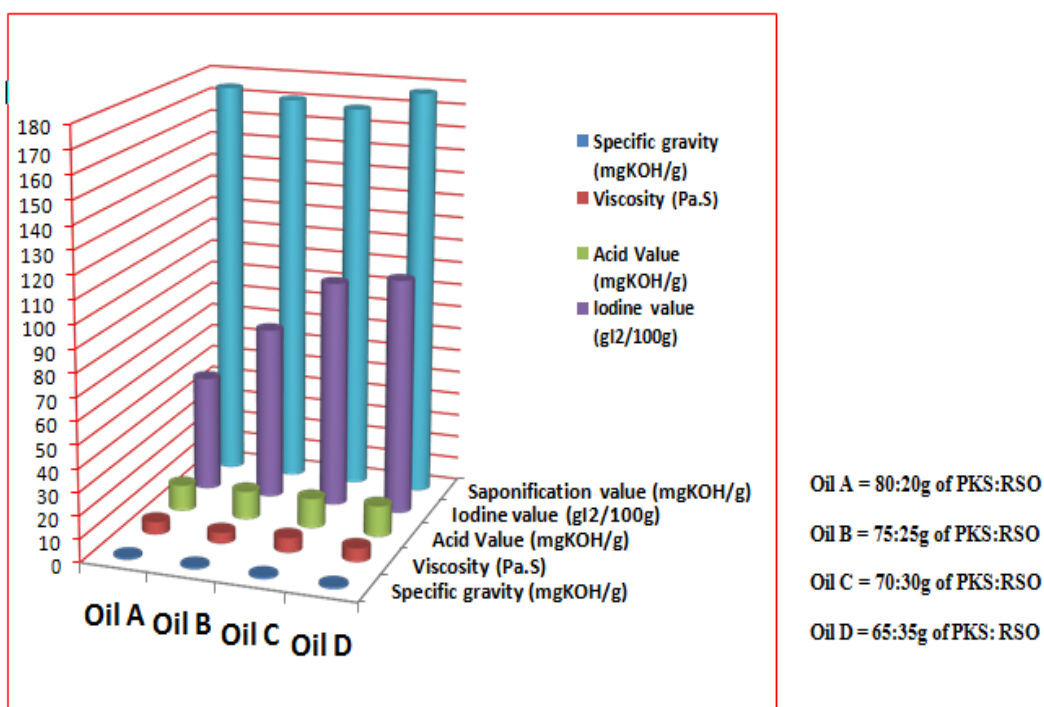


Figure2: The GC-MS result of the palm kernel stearin (PKS)

**3.2 Characterization of different ratios of dehydrated palm kernel stearin –Rubber Seed oil mixture:**

Figure 3 shows the characterization of the Oil A, Oil B, Oil C and Oil D, from the figure, it was observed that the specific gravity of the four oils (0.8,0.81,0.84& 0.83) were less dense than water which classified the oil to be within the comparable standard in the production of the alkyd resin [8]. Also from figure, there was an increase in the iodine value from oil A to oil D which indicates increase in the unsaturation level of the palm kernel stearin through modification of its pendent chain with the percentage of rubber seed oil. The iodine value of the Oil C and Oil D indicates that the level of unsaturation in the oil will accommodate the cross-linking reaction of the resultant alkyd to form auto-oxidative alkyd (dry and hard solid films) [8]. From the figure, the oils has different acid value and this can be attributed to the hydrolytic reaction during the dehydration of the oil blend [9]. Generally the acid value is used to measure the level of deterioration of the oil. The saponification values of the different oil were also shown in the figure and this reveals the average molecular weight of the fatty acids of triglycerides present in the four oils.



**Figure3: Characterization of the Oil A – Oil D**

**3.3 Characterization of the Alkyd Resin**

The Characterization of the four different medium oil length palm kernel modified alkyd resin produced compared with medium oil length cotton seed oil modified alkyd resin (CSO alkyd) [10] which serves as a reference alkyd resin is shown figure 4. From the figure, a significant increase in the iodine value from alkyd A down to Alkyd D was observed which shows the level of unsaturation in the modified alkyl resin increases with the increase in the rubber seed oil ratio content in the modified palm kernel stearin used in the synthesis of the alkyd resin. Comparing with the reference alkyd, the Alkyd C and D exhibit a comparable iodine value with the CSO Alkyd[10] which makes them semi drying oil modified resin. The saponification values of the synthesized (Alkyd A – Alkyd D) was also within the acceptable limit [11] and were found to be higher than the saponification value of the triglycerides oils used in modifying them and this may be attributed to the polymerization reaction during the formation of the alkyds which made them essentially polyester. It was also observed that the acid values of the four alkyds were relatively low making them preferred binder for paint production since higher acid value of binders would contribute to corrosion [12]. Also, the viscosity of the alkyds produced were much higher to the viscosity of the oils used in producing them, and this is as a result of the formation of 3-dimensional structural in the cause of the reaction and the resistance of alkyd flow, which was brought about by intermolecular friction arising from increase in the molecular size [16].

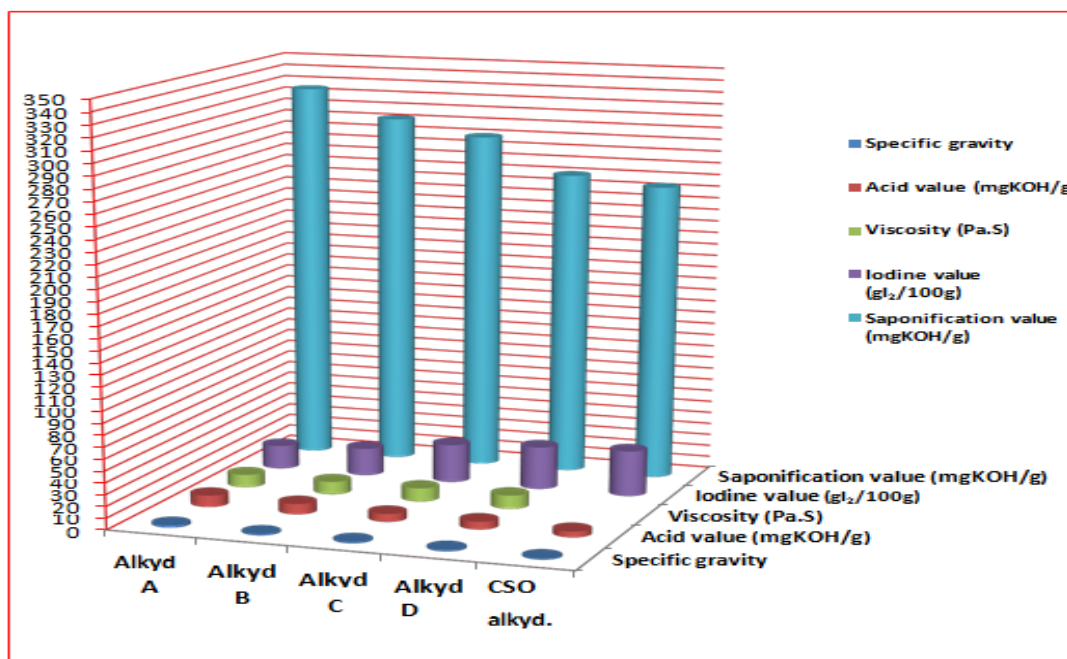


Figure 4: The characterization of the synthesized alkyd resin compared with the reference alkyd[10]

### 3.4 The chemical resistance of the Alkyds films

The Chemical resistance of the four different medium oil length palm kernel stearin modified alkyl resins were determined in three media; distilled water, 0.1 moles of sodium hydroxide and 0.1 moles of Hydrochloric acid. Table II shows that the alkyd C and alkyd D has good chemical resistance properties in the three media when compared to the alkyd A and B. From the table, it was observed that there is no change/ effect on alkyd resin C and D after immersion on distilled water and 0.1moles of HCl for a period of 18hours unlike alkyd A whose film got whitening after immersion on distilled water after 18 hours, Also the film of the alkyd A and alkyd B got whitening after 6 and 12 hours respectively when immersed in 0.1 moles of HCl. When the four alkyds were in immersed in 0.1 moles of NaOH, alkyds A and B films got whitening after 6hours whereas alkyds C and D films got whitening after immersion period of 12hours. From the result, it shows that none of the alkyds has a perfect resistance to the alkali solution though alkyd C and D has a better chemical resistance in alkali solution compared to alkyd A and B because it takes longer time before its film got whitening. In summary, the result shows that alkyd C and D has a very good chemical resistance.

TABLE II: Chemical resistance of the alkyds film as determined after air dried for 48hours.

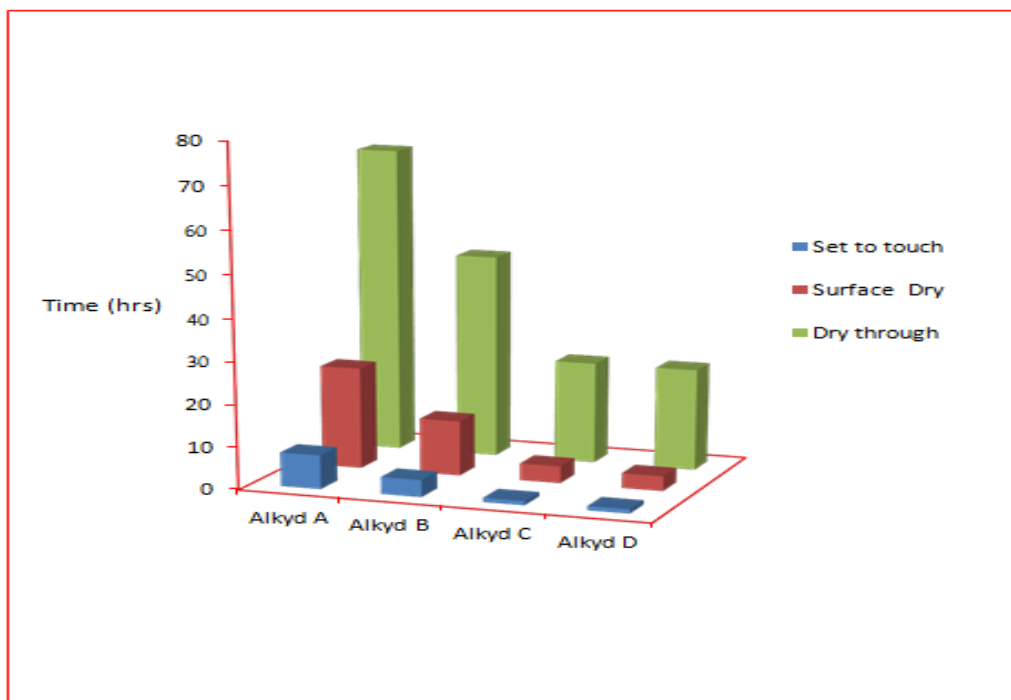
Alkyl Resin		Alkyd A	Alkyd B	Alkyd C	Alkyd D
Media	Immersion time (hours)	Appearance of the film	Appearance of the film	Appearance of the film	Appearance of the film
Distilled water	6	4	4	4	4
	12	4	4	4	4
	18	1	4	4	4
0.1moles NaOH	6	1 and 2	1	4	4
	12	3	2	1	1
	18	3	3	3	3
0.1moles HCl	6	1	4	4	4
	12	2	1	4	4
	18	3	3	2	4

1= Whitening, 2=Blistering, 3=Removal, 4=No effect



**3.5 The Drying Schedule of the Alkyd A – Alkyd D**

The Alkyd A – Alkyd D were each hand coated on the surface of four different aluminum plates which were cleaned with an ethanol to make sure that the surface of the aluminum plates were free from impurities/contaminants which might alter the drying test carried on it. The results of the drying time of the alkyd A to D at indoor temperature of 32°C±2 are shown in Figure 5. The results shows that marginal improvements were observed in the both set to touch, surface dry and dry through time from alkyd A to Alkyd D which shows that the drying schedule of an alkyds is generally based on the degree of unsaturation of the oil used in the synthesis of the alkyd and other factors such as sunlight, temperature of the drying as well as the volume of the oxygen [13] but the drying schedule of the alkyd film in this research was achieved through the process of auto-oxidation involving the adsorption of oxygen at the double bond of the synthesized alkyd which was made possible by unsaturated nature of the oil used in the synthesis of the alkyd. It can be inferred that alkyd C and D could be used as a binder in surface coating formulations as it showed comparable coating properties (drying time) to other reported oil modified alkyd [14]. The acid value and carboxyl functionality (F-COO) have effect on drying time of the resin. As observed from Fig 4, Alkyd C and Alkyd D which have relative minimal acid value when compare to Alkyd A and Alkyd B have the best drying properties.



**Figure 5: Chart showing the drying schedule of alkyd A – alkyd D**

**3.6 Mechanical properties of Alkyd A – Alkyd D**

From the Table III, it can be inferred that the four medium oil length palm kernel stearin alkyd resin produced exhibits a good mechanical properties when subjected to impact, adhesion and scratch hardness test and this may be attributed to the exhibition of good viscosity properties by the alkyds.

**TABLE III: Mechanical Properties of the Alkyd A – Alkyd**

Alkyd Resins	Mechanical Test		
	Impact test	Adhesion Test	scratch hardness test
Alkyd A	Passed	Good	H Passed, 3H Passed
Alkyd B	Passed	Good	H Passed, 3H Passed
Alkyd C	Passed	Good	H Passed, 3H Passed
Alkyd D	Passed	Good	H Passed, 3H Passed

3.7 Kinetic Results

TABLE IV: Kinetic tables for the synthesized Alkyds.

Time (mins)	Alkyd A					Alkyd B				
	$\mu$	$\mu^2$	$\ln\mu$	$1/\mu$	$1/\mu^2$	$\mu$	$\mu^2$	$\ln\mu$	$1/\mu$	$1/\mu^2$
30	2.54	6.45	0.93	0.39	0.16	1.95	3.8	0.67	0.51	0.26
60	5.86	34.34	1.77	0.17	0.03	3.62	13.1	1.29	0.28	0.08
90	7.27	52.85	1.98	0.14	0.02	5.88	34.57	1.77	0.17	0.03
120	7.42	55.06	2	0.13	0.02	6.99	48.86	1.94	0.14	0.02
150	8.06	64.96	2.09	0.12	0.02	7.23	52.27	1.98	0.14	0.02

Time (mins)	Alkyd C					Alkyd D				
	$\mu$	$\mu^2$	$\ln\mu$	$1/\mu$	$1/\mu^2$	$\mu$	$\mu^2$	$\ln\mu$	$1/\mu$	$1/\mu^2$
30	2.63	6.92	0.97	0.38	0.14	2.85	8.12	1.05	0.35	0.12
60	2.70	7.29	0.99	0.37	0.14	3.33	11.09	1.20	0.30	0.09
90	4.00	16.00	1.39	0.25	0.06	4.54	20.61	1.51	0.22	0.05
120	5.56	30.91	1.72	0.18	0.03	6.25	39.06	1.83	0.16	0.03
150	11.52	132.71	2.44	0.09	0.01	11.57	133.86	2.45	0.09	0.01

Kinetic models of the synthesized alkyd samples using viscosity as a function of time during the poly-esterification reaction were investigated using regression analysis and executed using Microsoft excel program 2010. In order to determine the order of the reaction for each of the synthesized alkyds, a linear fit was applied to the plotted experimental data for the first, second and third order plot for the test of reaction order and in each case, the rate constant (k) and the coefficient of determination ( $R^2$ ) was determined and the tested order of reaction with the highest value of  $R^2$  that is “coefficient of determination” is the order of the reaction for that particular alkyd sample.

The plot for the test of kinetic order reaction shown in figure 6 below shows the kinetic order of reaction and rate constants obtained for the synthesized alkyds as follows; Alkyd A - first order kinetic model with rate constant of 0.0119/mins, Alkyd B – first order kinetic model with rate constant of 0.0136/mins, Alkyd C – second order kinetic model with 0.0026 (Pa S)<sup>-1</sup>/ mins, Alkyd D – second order kinetic model with 0.0022 (Pa S)<sup>-1</sup>/mins which is evidence in the value of their respective coefficient of determination ( $R^2$ ). The rate of reactions obtained for the alkyds were based on the change in the viscosity (increase in viscosity) as a result of consumption of the carboxylic functionality (decrease in acid value) during the polymerization reaction. Alkyd C has the highest rate constant when compared to the other three alkyds and this shows that the esterification reaction during the synthesis of Alkyd C occurs at a faster rate when compared to others [19]. The change in reaction order from first order kinetic for Alkyd A and Alkyd B to Second order kinetic model for Alkyd C and Alkyd D may be attributed to variations in temperature ranging from 230°C to 250°C during the esterification process of the alkyds because at a lower temperature, oxygen containing components builds – up and at a higher temperature, carbon-oxygen and carbon-carbon linkages are formed [18]. Also the change in reaction order between (Alkyd A & Alkyd B) and (Alkyd C & Alkyd D) can be attributed to the structural modification of the palm kernel stearin chain with rubber seed oil. This modification introduces an appreciable increase in the level of unsaturation

(double C=C) in the oil mostly for Oil C and Oil D as seen in their respective iodine value in figure 4 and some of this double bond of the oil may not be available during the esterification process, thus change in kinetic model when compared to the more saturated oil A and Oil B.

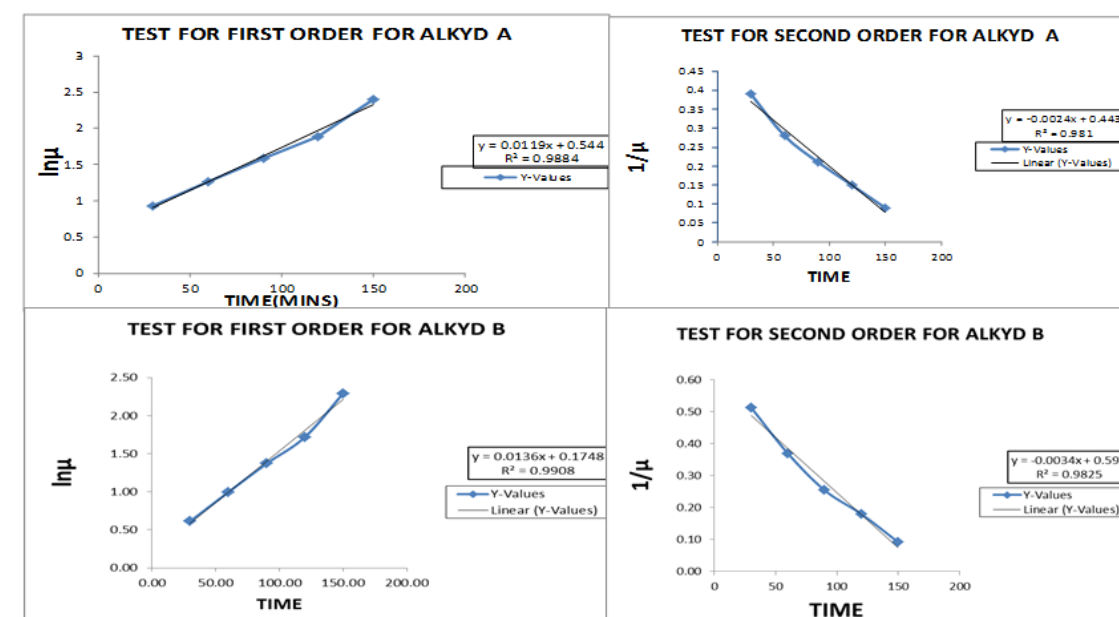
When compared to the similar work done in the literature, it was observed that the rate constant and reaction kinetic model obtained for the Alkyd C and Alkyd D are in a reasonable agreement with result obtained for the kinetic study of the styrenated palm oil based alkyd [19].

From the kinetic plot (figure 6), A deviation from linearity was observed at later stage of the reaction for the Alkyd A and Alkyd B; whereas deviation from linearity was observed at early stage for Alkyd C and Alkyd D. These deviations can be attributed to the occurrence of chain branching during the formation of 3-dimensional structure of an alkyd resin during the polymerization reaction.

The variations in the value of the rate constant of the synthesized alkyd samples: Alkyd A, Alkyd B, Alkyd C, and Alkyd D based on the discussion above can precisely be attributed to the proportion of the reactants used, speed of agitation of the reaction mixture, changes in temperature and removal of water of esterification, these factors jointly represents the viscosity of the alkyd system [2].

Also it is important to note that the complexity nature of the alkyd polymerization mechanism and unstable natures of the monomers structures in the alkyd resins has really pose a serious challenges to the researchers in the area of determining a detailed kinetic model that can really predict the reaction motion and product quality in alkyd reactor. Though many works has been done on the kinetic study of the alkyd resin synthesis, but the results has really been a subject of disagreement among research workers.

Aigbodion and Okieimen [2] did a research studies on the kinetics of the preparation of rubber seed oil alkyd and found out that the initial reaction rates follow second order kinetics with deviation at the later stage of reaction but Igwe and Ogbobe [15] carried out a similar research on the kinetic study on alkyd resin synthesis, using melon seed, rubber seed oil, linseed and soyabean oil and the results showed that poly-esterification reactions did not follow a second order kinetics during the early part of the reaction and this contradict the result of Aigbodion and Okieimen. Also Ekpa O and Isaac I [12] did carried out similar study using coconut, soybean and palm kernel oil and the studies showed that the poly-esterification reactions follow a second order kinetics with slight deviation from linearity at the beginning of the reaction. These problems of contradictions of results in determining a suitable kinetic model to predict the exact kinetic order of reaction for the poly-esterification reaction during the synthesis of alkyd resin has been well-emphasized in reaction engineering literatures and no satisfactory solution has been reported.



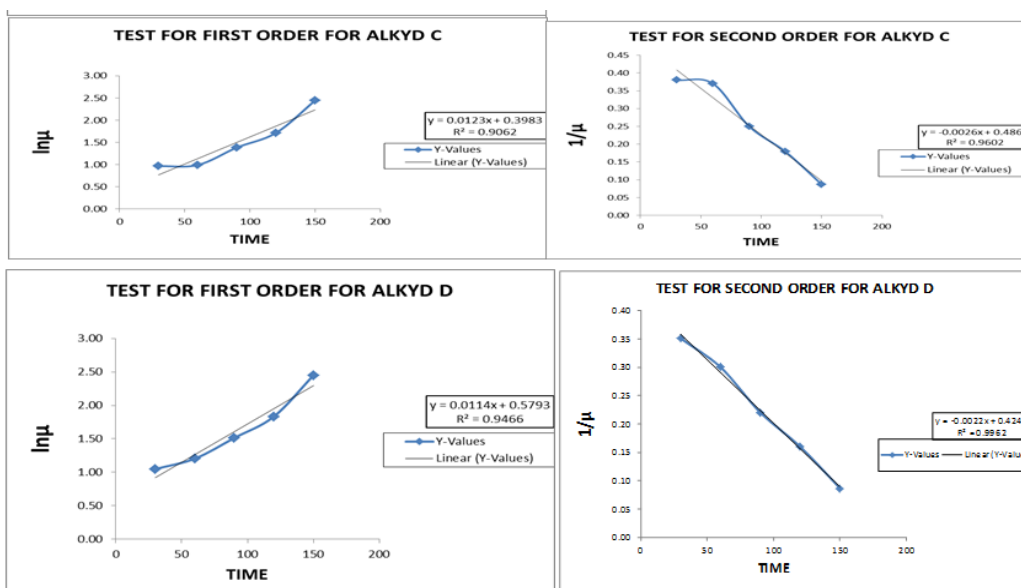


Figure 6: Kinetic plot for test of order of reaction for the poly-esterification process of the synthesized alkyds.

- None of the tested alkyds samples followed third order kinetic model, so the plot for the third order kinetic model test was not included.

Table 6: Kinetic model characteristics of the synthesized alkyds.

Alkyd Samples	Kinetic model characteristics		
	Reaction order	Reaction rate	R <sup>2</sup>
Alkyd A	1ST ORDER	0.0119/min	0.9884
Alkyd B	1ST ORDER	0.0136/min	0.9908
Alkyd C	2ND ORDER	0.0026 (Pa.S) <sup>-1</sup> /min	0.9602
Alkyd D	2ND ORDER	0.0022 (Pa.S) <sup>-1</sup> /min	0.9962

#### IV. CONCLUSION

The investigative study of optimum unsaturated fatty acid content of palm kernel stearin for the synthesis of an auto-oxidative modified palm kernel stearin based alkyd resin shows that the Alkyd C yield the best result. This means that 70:30 wt. % oil ratio of Palm Kernel Stearin to Rubber Seed Oil is the desired oil blend ratio. The result of the kinetic study of the poly-esterification reaction of the synthesized alkyds shows that alkyd A and alkyd B follows first order kinetic reaction model with rate constant of 0.0119/mins and 0.0136/mins whereas alkyd C and alkyd D follows second order kinetic reaction model with rate constant of 0.0026 (Pa S)<sup>-1</sup>/ mins and 0.0022 (Pa S)<sup>-1</sup>/ mins respectively.

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