Kinetics Study of Cottonseed Oil Modified Alkyd Resin Poly-condensation

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Abstract

An appropriate kinetics law that governed some important conditions of the reaction process for cotton seed oil modified alkyd resin has been developed. Kinetics experiments were conducted following a standard procedure. The classical third order conversion rate model was adopted in determining the rate parameters while the viscosity-conversion model suggested by the free-volume theory was applied for the viscosity kinetics studies. The kinetics models considered for this study adequately predict the reaction progress even beyond the actual gelation point. The effects of the system parameters on both the predicted yields and the corresponding conversion rates were documented in a well-designed partial sampling space implemented by statistical optimization paradigm. The effects of system parameters on the reaction rates further investigated based on Arrhenius equation detects a heavy mass transfer resistance during the esterification process. A detailed analysis of the response reveals a deviation from linear first order kinetics and possible transition to second and higher order kinetics in the later stages of the esterification reaction.

Keywords: Polycondensation reaction, kinetic model, nonlinear fit, free-volume theory, Arrhenius equation.

1.0 Introduction

Esters have gained wide applications in the contemporary daily living and chemical industry, such as plasticizers, fragrance, adhesive and lubricants [1], [2]. The vast majority of esters can be prepared using esterification reaction which has acquired further improvement from the engineering side mainly due to researches on esterification kinetics. In the surface coating industries, oil-modified polyesters or alkyds resins dominates as the most widely used solvent- borne binder [3]. The polyester is derived from a poly-condensation reaction between a polyhydric alcohol and a polybasic organic acid as seen in (1)

$$\boldsymbol{Alcohol}\ (\boldsymbol{-COH}) + \boldsymbol{Acid}\ (\boldsymbol{-COOH}) \rightarrow \boldsymbol{Ester}\ (\boldsymbol{-COOC-}) + \boldsymbol{Water}\ (\boldsymbol{H_2O}) \qquad (1)$$

These low molecular weight esters are very flexible and versatile and have been found to be compatible with other polymer systems [4], [5].

Cottonseed oil has been found to be a sustainable material for alkyd resin synthesis in terms of its availability and renewability. Castor oil modified alkyd resin has also been developed keeping two criteria in mind; the resin met all the technical and industrial standards of durability, fastness to exposure, resistance to chemical, etc., and, met all the ecologically relevant standards. [6], [7], [8]. Cotton seed oil has been classified as semi-drying oil and owe its value as raw materials for decorative and protective coatings to the ability to polymerize or "dry" after they have been applied to a surface to form tough, adherent, impervious, and abrasion resistance films. The advantages claimed in surface coating applications include excellent odor, good drying properties, more uniform polymer structure, and lack of after-yellowing. The dehydrated cotton seed oil is non-yellowing oil and so can meet requirements of coating industries [9], [10], [11], [12], [13].

Many significant efforts have been made to increase alkyd resin production through researche different for material and methods for alkyd resin preparation. Aigbodion et al [14] studied enhancing the quality of alkyd resins using methyl esters of rubber seed oil in 2004. Hlaing and Mya, [7] studied the manufacture of alkyd resin from dehydrated castor oil. In these various reports, the possibility of attaining a gelation point which is a menace in alkyd resin production was emphasized.

In order to design an efficient batch reactor for alkyd resin production from cotton seed oil, a suitable kinetic mechanism and reaction rate constants must be found. The processing technique adopted in this research involves the basic trans-esterification process achieved through alcoholysis-esterification interface, popularly known as the mono-glyceride process in which the fear of increasing the production cost was alleviated through standard parameter optimization paradigm.

In the scheme, the triglyceride oil was first converted to intermediate product (monoglyceride) which is subsequently esterified in presence of phthalic anhydride (PA) as

illustrated in figure 1. The detailed optimization procedure applied to the production of the oil modified alkyd resin has been reported in [15]. There is no reported detailed kinetic report on the production process. In fact, the existing alkyd kinetics studies [16], [17], 18], [19] reported simplified or lumped condensation-type kinetic models which are valid either at low or high conversion. The central focus of this research, therefore, is to develop appropriate kinetic laws that govern some important conditions of the reaction process based on standard parameter optimization procedures. A general predictive model was equally developed for the system responses ($Y_{acid\ value}$ and $Y_{viscosity}$) as a major objective of the study, employing multivariate regression analysis conducted with respect to the identified system variables. The rate at which the process is executed is known to depend on the interactions of system parameters like reaction temperature (A), process duration (B), PA/oil ratio (C) and catalyst concentration (D).The multiple regression analysis sampling space is shown in table 1, which depicts adequate range of the system parameters for process optimization as derived from a standard preplanning operation involving steepest ascent.

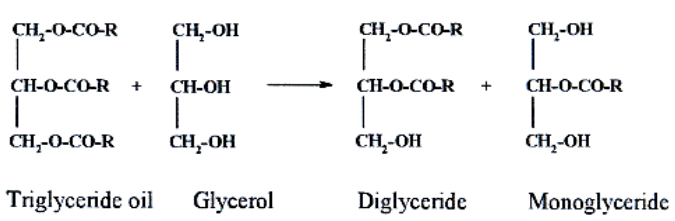
The proposed kinetics modeling adopts a simple but appropriate technique in which data obtained from the partial sampling procedure described by multivariate regression are fit to a reduced order reaction kinetics model, relating the reaction rate to the initial concentration of the reactants (a) and (b). The concentration of the mixture at later time (x) and the rate constant (k) are as follows;

$$Rate\ dx/_{dt} = k(a-x)(b-x) \qquad (2)$$

Also, the estimation of the unknown parameters of the generalized models involves some standard linearization techniques and the popular nonlinear least squares approximation algorithm.

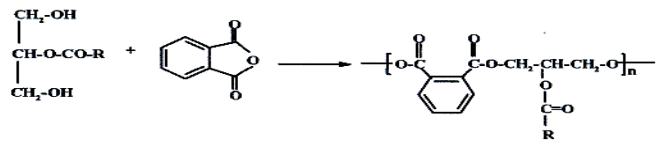
Subsequently, the resulting rate parameters were applied to the popular Arrhenius equation (3) through the nonlinear least square algorithm for evaluation of the thermodynamic variables which includes the activation energy (ΔE) and frequency factor (A).

$$k = A\ exp(-\Delta E/RT) \qquad (3)$$



First stage (alcoholysis)

Figure1:Two-phase polymerization reactions



Second stage (esterification).

Figure1:Two-phase polymerization reactions of the monoglyceride process

2.0 Materials and Methods

2.1 Materials

Cotton seed oil was extracted by solvent extraction in soxhlet equipment at the Chemical Engineering Laboratory of Institute of Management and Technology, Enugu, Nigeria. A rotary evaporator equipped with digital thermometer, rotatable round bottom flask, condenser and water were also used. Other equipment include; electronic weighing balance, heating mantle, magnetic stirrer and general laboratory glassware.

Phthalic anhydride ($C_6H_4(CO)_2O$) with minimum assay > 97%, glycerol ($C_3H_8O_3$) with assay > 99%, sodium bisulphate ($NaHSO_4$) with assay 97.5% and Lead(II) Oxide (PbO) with assay > 96.8% were purchased from BDH chemicals ltd, Poole, England. Diethyl ether, ethanol, xylene, anhydrous methanol, sodium hydroxide (NaOH) with assay 96%, was supplied by wharefedale laboratories, Yorkshire, England. The chemicals purchased were of highest purity.

2.2 Experimental

In the synthesis of the alkyd resin, two stages were involved. The first stage was alcoholysis and the second stage esterification. The basic reagents utilized for the coupled operations include dehydrated oil, glycerol, phthalic anhydride (PA) and catalyst (PbO+NaOH). The method suggested by Hlaing, [7] for alkyd resin synthesis is utilized to implement a central composite rotatable design, formulated based on the factor setting indicated in table 1. The details on the experimental design may be found in [15]

Alcoholysis: In this stage, Mono-glyceride was first synthesized by reacting the dehydrated oil with glycerol. The oil was heated maintaining agitation speed of 700 rpm. Glycerol and selected catalyst (0.1% PbO + 0.2% NaOH) wt was added and alcoholysis reaction was allowed to progress

at 230-240°C. The reaction was continued until a sample of the reaction mixture became soluble in 2 to 4 volume of anhydrous methanol. After alcoholysis was completed, the reaction mixture was cooled to 140°C

Esterification: At this stage, phthalic anhydride was added to the mono-glyceride mixture. The temperature of the mixture was maintained at the range of 220 – 260°C as shown in table 2. This second stage reaction is continued at constant temperature and long chain molecules were formed which contain excess hydroxyl group. At this state water was released. Removal of water from the mixture was facilitated by a solvent extraction method. The mixed vapor generated was then condensed and collected. Xylene was suitably applied for this process considering its boiling point and solubility in water. The reaction progress was monitored by intermittent measurement of the AV, viscosity and water off. The data for the detailed kinetics study was gathered towards the end of the reaction when acid conversion approaches 87%. The acid value (AV) and viscosity were measured off-line for all reaction durations after a uniform delay period of 30minutes. The conversion of alkyd resin(Y) calculated analytically in terms of measured reduction in AV (1) for a given reaction phase using equation 2, relying on data obtained from normal titration while the viscosity was measured instrumentally for cold sample using viscometer.

Table 1 Formulation of coded variables for experimental analysis

Independent variable	Range and level				
	$-\alpha$	-1	0	1	α
Temperature (Celsius) (A)	220	230	240	250	260
Time (minutes) (B)	30	60	90	120	150
Molar ratio (C)	0.1:1	0.2:1	0.3:1	0.4:1	0.5:1
Catalyst concentration (wt %.) (D)	0.02	0.04	0.06	0.08	0.10

Table 2: Typical range of independent variables for Alkyd Resin synthesis.

Temp.(°C)	PA/Oil Ratio	Glycerol (wt. %)	Reaction time (min)	Catalyst (wt. %)
220-260	0.1-0.5	17.6	30-150	0.02-0.1

The extent of reaction or conversion (Y) is estimated from the end group analysis of the aliquots of the reaction mixture withdrawn at 30 minutes interval.

$$Acid\ \ value(AV) = \frac{MV \times 40}{W} \qquad (4)$$

$$Y = 1 - {AV_j}/{AV_0} = 1 - {V_j}/{V_0} \qquad (5)$$

AV_0 and AV_j are the acid values of the mixture determined at the initial time (t=0) and later time t=j respectively while V_0 and $V_j$are the corresponding volumes of $NaOH_{(aq)}$ used in the titration.

2.3 Kinetics modeling for the polycondensation reaction

The kinetic model used in this work relied on the following assumptions:

(i) The esterification reaction was a reversible heterogeneous process, the rate of which was controlled by that of the chemical reaction. (ii) The chemical reaction occurred in the oil phase. (iii) PA was the limiting reactant. (iv) Monoglyceride concentration was assumed constant during the process.

Under these conditions, the reaction was assumed to be pseudo-homogeneous, first-order in the forward direction and second-order in the reverse direction, and hence conform to the following kinetic laws:

$$A \underset{K_2}{\overset{K_1}{\longleftrightarrow}} C + D \qquad (6)$$

$$\frac{-dA}{dt} \equiv K^*{}_1[A] - K^*{}_2[C].[D] \qquad (7)$$

Where;

[A] denotes the concentration of acid in the reacting system (i.e. the acid value)

[C] and [D] are the concentrations of ester and water respectively, formed during the reaction.

$K^*{}_1$ and $K^*{}_2$ are the kinetic constants for the forward and reverse reactions respectively.

If [D] and [C] are assumed to be zero at the start (t = 0), and $A = A_0 - E$ (E being the acidity removed), then, according to Carberry [19].

$$\frac{-dE}{dt} \equiv K_1(A_0 - E) - K_2E^2 \qquad (8)$$

A_0 is the initial acid number determined prior to the reaction

If the forward reaction is of primary interest as indicated in the objective of the current research, the second order term of the rate equation (8) may be ignored and the equivalent first order rate equation becomes;

$$\frac{-dE}{dt} \equiv K(A_0 - E) \quad (9)$$

On integration we have;

$$-ln(A_0 - E) = -\ln(1 - Y) = K^*t + \gamma \quad (10)$$

Or

$$Y = 1 - e^{-(K^*t+\gamma)} \quad (11)$$

$$E = A_0 - A \; and \; Y(conversion) = E/A_0 \quad (12)$$

The generalized first order kinetics constant K^* and the constant of integration γ were derived from the gradient and the intercepts of the linear plot of $-\ln(1-Y)$ corresponding to the forward process and the goodness of fit of the resulting model was tested numerically using the calculated norm of residuals(ε_N). The general predictive model which was developed for the system responses ($Y_{acid\ value}$ and $Y_{viscosity}$) follows the method described in [15].

2.4 Conversion kinetics theory

One of the empirical relations applicable in the coating industry is the 3rd-order reaction rate equation of acid functional group conversion (13).

$$r = k(1-c)(c_e - c)^2 \quad (13)$$

From standard kinetic modeling perspective, the reaction rate model (13) could be made to adequately describe the entire course of reaction by assuming a time varying reaction rate parameter as follows;

$$k(t) = \kappa(c(t), T(t)) \quad (14)$$

which depends on variables like c and T.

If the batch can operates at constant temperature

$$\frac{dc}{dt} = r(c, k, c_e) = k(1-c)(c_e - c)^2 \quad (15)$$

To simplify the integration of the third order conversion dynamics (15) and enhance estimation of rate parameters, an equivalent first order model is written (16).

$$\frac{dc}{dt} = r(c, k, c_e) = K^*(t)(1-c) \quad (16)$$

From which the variables can be separated and integrated as follows;

$$\int \frac{dc}{1-c} = \int K^*(t)\, dt \quad (17)$$

$$-ln(1-c) = K^*t + \gamma \quad (18)$$

i.e. $c = 1 - e^{-(K^*t+\gamma)}$ (19)

Hence, $Y = 1 - e^{-(K^*t+\gamma)}$

The generalized first order kinetics constant $K^*$and the generalized integration constant γ can then be estimated from the gradient and the intercepts of the linear fit to the plot of $-\ln(1-c)$ against time t. The adequacy of the linear fit may be monitored numerically using the statistically calculated norm of residuals ϵ_N or coefficient of determination (R^2).

2.5 Viscosity kinetics theory

The study of reactor kinetics based on viscosity measurement was carried out using viscosity conversion relation suggested by the classical free-volume theory [20]. The parameter estimation procedure was formulated in a non-linear least squares fashion. This approach requires initial guess of the model parameters.

$$v = \mu(c, p_\mu) = a_\mu e^{b_\mu/(c_\mu - c)} \quad (20)$$
$$p_\mu = [a_\mu, b_\mu, c_\mu]'$$

3.0 Results and Discussion.

The rate of a step polymerization is most conveniently expressed in terms of the concentration of reacting functional groups. Thus, the poly-esterification was experimentally monitored by titrating for the unreacted carboxylic group with a base at every time step. Titration continues even after attaining a conversion of more than 87% towards the end of the poly-condensation process. The results show that the identified variables were significant. The present kinetics study accounts for these major process parameters. Although the experiments were conducted in actual units of the variables, the result presentation and data analyses preferably adopt coded and un-coded notation for simplicity. A constant experimental delay period of 30minutes was utilized and at every time step, the conversion and cold viscosity of the emerging product were measured offline. The performances of the proposed reduced third order conversion model (17) and the free-volume type conversion-viscosity model (21) for time prediction of reaction progress and emerging product quality are tested for the pilot plant based on the experimental data.

3.1 Parameter estimation

The estimation of the rate constant k follows a linearization approach that results in equation (10) as described in section 2.3. The total allowed reaction period T considered to be zero (0) in the beginning of the monitoring was plotted against $-\ln(1-c)$ shown in figure 2. The resulting gradient and

intercept of the linear fit to the experimental data corresponds to the desired parameter estimates (12).

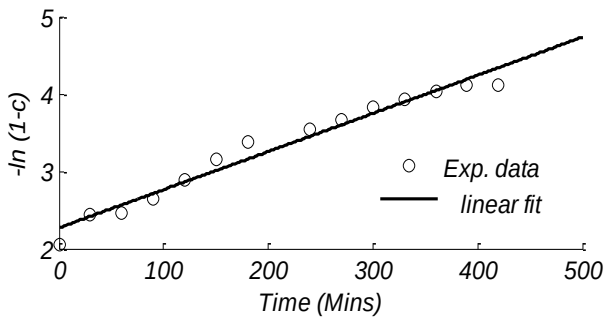


Figure 2: Linear estimation of the generalized rate constant K^* using the time evolution of the unconverted acid group.

$$-ln(1-c) = K^*t + \gamma \equiv 0.00493t + 2.2688 \qquad (21)$$

Norm of residuals $\epsilon_N = 0.46089$

Nonlinear least square fit

This is a relevant theory for constructing a mechanistic model which is nonlinear in the unknown parameters. It involves iterative procedure that starts with an initial guess of the unknown parameters. The subsequent iterations alter the current guess until the algorithm converges. This method also involves selecting the field function(s) or the mechanistic model(s) that would provide adequate fit to the experimental data.

The functions for fitting nonlinear models are of the form

$$y = f(X, \beta) + \varepsilon \qquad (22)$$

Where:

y is an-n by-1 vector of observations

f is any function of X

X is an n-by-p matrix of input variables

β is a p-by-1 vector of unknown parameters

Using the iterative method described, the unknown nonlinear parameters of the free-volume type conversion-viscosity model (20) was estimated as

$$p_\mu = [a_\mu, b_\mu, c_\mu]' = [8.4029, 0.5689, 1.1345]' \qquad (23)$$

3.2 State estimation of conversion and viscosity

The results of the state estimation of the acid conversion presented in figure 3 shows a good correspondence between the experimental data and those predicted by the proposed conversion kinetics model. The completion of the esterification process at which the operation of the batch may be stopped is established as the conversion value gets sufficiently close to 1 (i.e. 100%). This conforms to a total monitoring period greater 300 minutes. However, the batch operation cannot be stopped without adequate consent to other product quality indicators like viscosity and gelation.

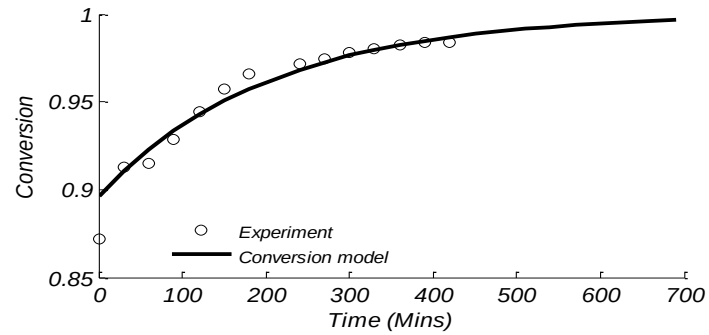


Figure 3: Experimental and predicted conversion profile of the alkyd reactor

The viscosity profile of the alkyd reactor presented in figure 4 also shows substantial agreement between the experimental and the predicted data. An important observation recorded in this figure is the sustained increase in the viscosity of emerging product as the cumulative delay period increase which emphasizes the need to mark out a critical gel point about which the operation of the batch must be stopped to ensure quality product. Nevertheless, selecting what is desirable in terms viscosity may vary depending on certain established standards and professional recommendation. The application of viscosity-conversion model proposed in this study for reactor monitoring guarantees one great advantage related with cost reduction on laboratory analysis since the on-line conversion measurement could be eliminated.

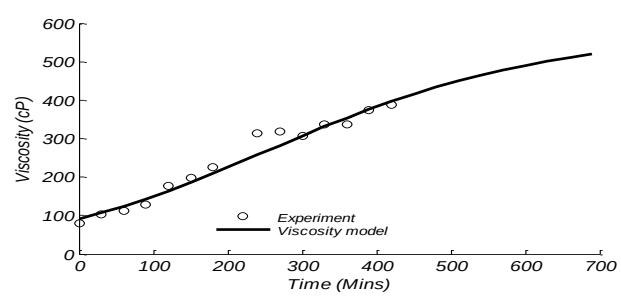


Figure 4: Experimental and predicted viscosity profile of the alkyd reactor.

3.3 Effects of process parameters

Equations (24-25) and Figures 5-7 disclose the predictive models for the responses ($Y_{coversion}$ and $Y_{viscosity}$) and the detailed effects of the system parameters on the rate of conversion analyzed in a partial sampling space presented in table1

$$Y_{conversion} = 79.82 + 7.64A + 10.14B + 5.42C + 5.20D - 3.79AB - 2.99BD - 3.85A^2 - 2.19B^2 - 2.82C^2 \quad (24)$$

$$Y_{viscosity} = 213 + 35.80A + 38.29B + 15.84C + 22.28D - 16.84AB - 16.39A^2 - 10.39B^2 - 9.31C^2 \quad (25)$$

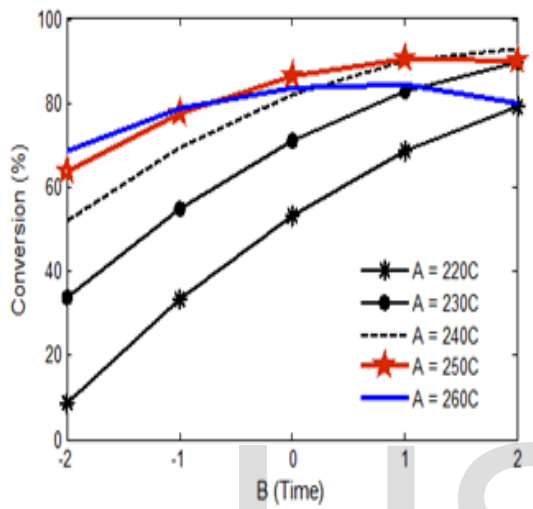


Figure 5: Effect of temperature on conversion rate

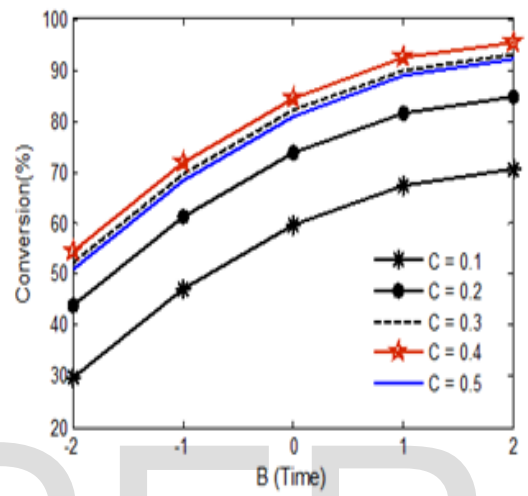


Figure 6: Effects of PA/oil ratio on conversion rate

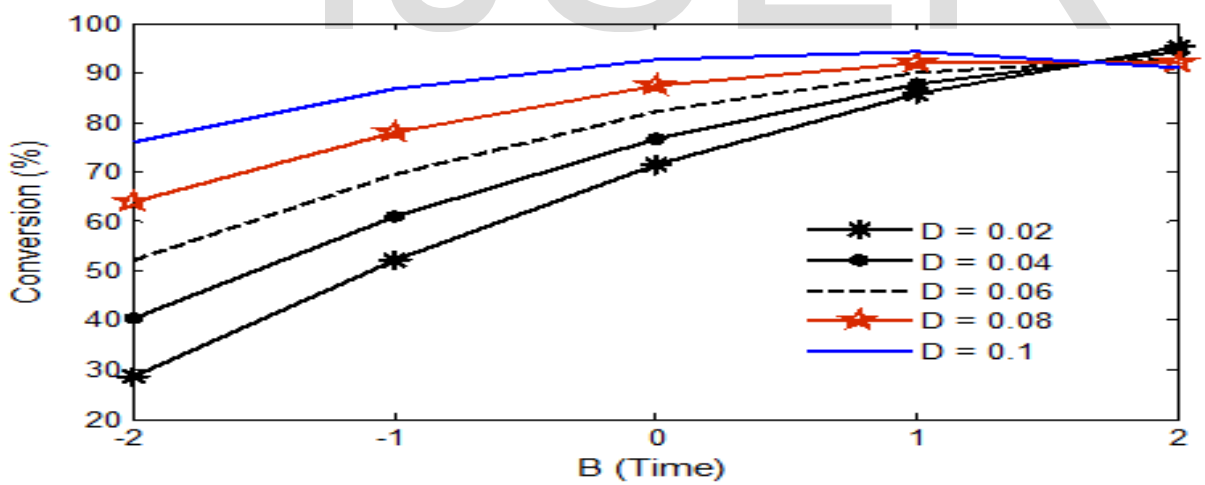


Figure 7: Effect of catalyst concentration on conversion rate

The study was approached by investigating the fall in AV (conversion) as a function of time within some economically viable settings of the other independent system variables. As expected for increased degree of unsaturation, it was observed that the rate of forward reactions were generally improved by slight upward adjustment of the PA/oil ratio up to C =1 while the reaction temperature (A) and catalyst concentration (D) assumed some fixed values. This observation is recorded in the linear rate plot of the experimental data presented in figures 8-10. It appeared that the rate of reaction of the polybasic acid (PA) with the primary hydroxyl groups of the monoglyceride to form linear polyesters was favored at the stated condition. This trend however reversed at C > 1 due to rapid depletion of the

primary hydroxyl group in excess of the acid which equally introduced curvature in the reaction path.

K^*	γ	ε_N	PA/oil ratio
0.2236	0.88507	0.1153	-2
0.3364	1.2898	0.1212	-1
0.4979	1.7226	0.0960	0
0.5921	1.9180	0.1136	1
0.4671	1.6513	0.1001	2

$A = 0; D = 0; r = K^*t + \gamma$

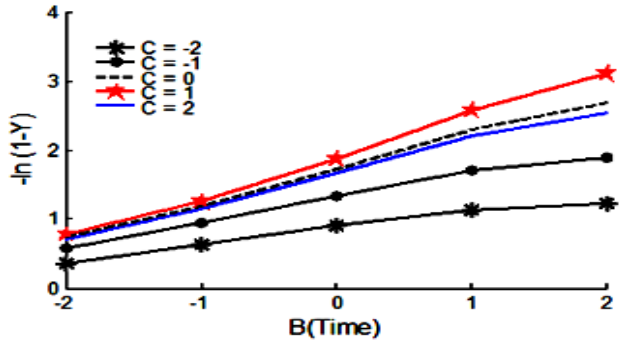


Figure 8: The analytical (a) and the experimental (b) kinetic model corresponding to T = 240⁰C

K^*	γ	ε_N	PA/oil ratio
0.2898	0.5697	0.0150	-2
0.3974	0.8977	0.0795	-1
0.5241	1.1858	0.2232	0
0.5818	1.3006	0.3145	1
0.5022	1.1412	0.1939	2

$A = -1; D = -1; r = K^*t + \gamma$

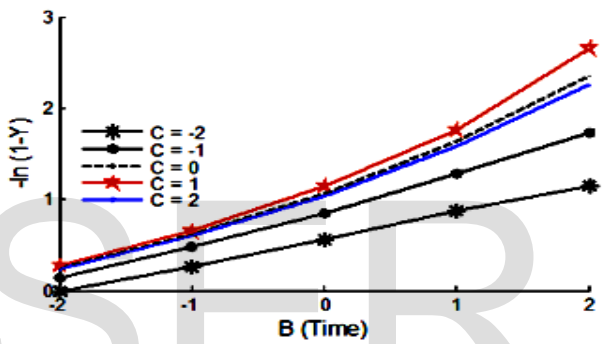


Figure 9: The analytical (a) and the experimental (b) kinetic model corresponding to T = 230⁰C

K^*	γ	ε_N	PA/oil ratio
0.3018	0.2549	0.0566	-2
0.3778	0.4836	0.1238	-1
0.4484	0.6576	0.2060	0
0.4756	0.7175	0.2429	1
0.4376	0.6328	0.1922	2

$A = -1; D = -1; r = K^*t + \gamma$

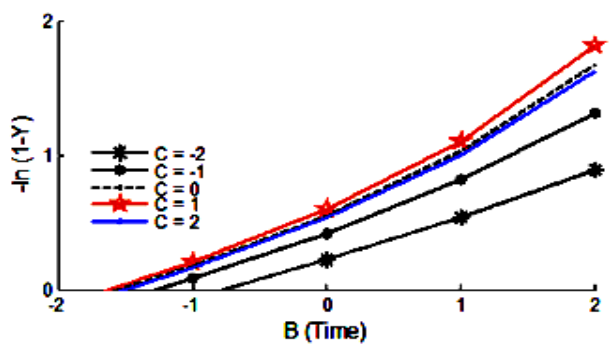


Figure 10: The analytical (a) and the experimental (b) kinetic model corresponding to T = 220⁰C

The study assumed that the forward reactions were satisfactorily described by a linear first order kinetic law of the general form

$$r = K^*t + \gamma \qquad (26)$$

This was particularly in the lower isotherms. The validity of the linear rate model within the optimum parameter range was however tested by evaluating the values of the coefficients K^* and γ of the rate equation such that an acceptable goodness of fit verified numerically with calculated norm of residuals(ε_N) is obtained between the result of (26) and the experimental data. The results presented

in figures 8-10 consistently returned low values of ε_N for each investigation step confirming good fit in the applicable space.

An important observation was the evolution of curvature in the reaction path towards the end of the forward process, which equally suggests a negative shift in the equilibrium position. Detailed study of the curvature in the present research shows that non optimal local inflexion points are possible at much higher isotherms (> 240⁰C). This equally explains the deviation from the more constrained linear type kinetic model to a robust quadratic model at elevated temperatures illustrated in figures 11 and 12. The decline in response noticed after the optimum reaction time has been explained on the concept of the secondary hydroxyl group which normally comes to play at the latter stage while the primary hydroxyl is varnishing. Molecules of PA possibly react with the secondary hydroxyls and connect the short chains to form complex, branched or network structures and in effect impedes the rate of forward process [20].

K_1	K_2	γ	ε_N	PA/oil ratio
-0.0626	0.0860	1.1775	0.0223	-2
-0.1022	0.1387	1.7885	0.0596	-1
-0.1666	0.2192	2.4681	0.1586	0
-0.2074	0.2673	2.8036	0.2443	1
-0.1538	0.2035	2.3501	0.1352	2

$A = 1; D = 1;\ r = K_1\, t^2 + K_2\, t + \gamma$

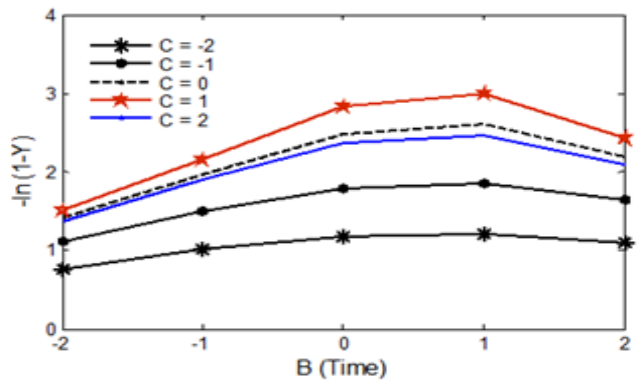


Figure 11: The analytical (a) and experimental (b) kinetic model corresponding to T = 250⁰C

K_1	K_2	γ	ε_N	PA/oil ratio
-0.0670	-0.1040	1.2747	0.0287	-2
-0.1152	-0.1775	1.9766	0.0869	-1
-0.2129	-0.3175	2.8951	0.3023	0
-0.3030	-0.4341	3.5102	0.6153	1
-0.1905	-0.2866	2.7159	0.2415	2

$A = 2; D = 2;\ r = K_1\, t^2 + K_2\, t + \gamma$

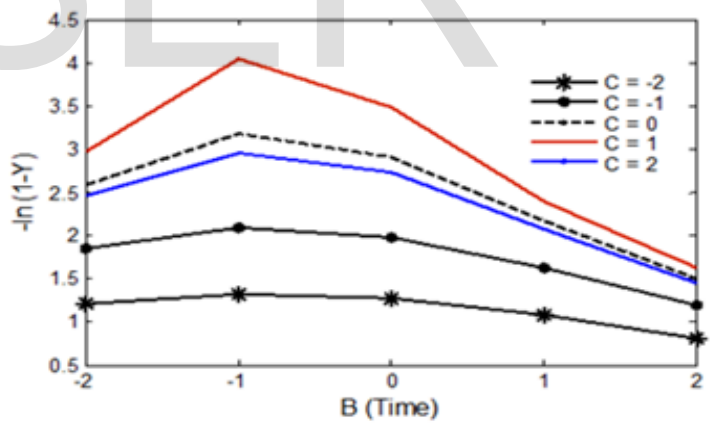


Figure 12: The analytical (a) and experimental (b) kinetic model corresponding to T = 260⁰C

The effects of PA/oil ratio on reaction rate was further investigated using the thermodynamic variables of the system supplied by the Arrhenius equation (2). The values of the frequency factor (A) and the energy term (ΔE) presented in table 3 were attained via non-linear regression implemented on the plots of lnk against T^{-1} for various PA/oil ratios shown in figure 13.

Table 3 Activation energies and frequency factors for castor oil modified alkyd resin synthesis

PA/oil ratio	-2	-1	0	1	2
A	0.1672	0.2466	0.3576	0.3954	0.3353
$\Delta E(kJ/mol)$	5.811	4.7564	3.4728	3.6449	3.7313

The validity of the linear type kinetic model in the forward process of esterification reaction is further demonstrated by comparing the alkyd resin conversions (Y) obtained with equation (24) derived from the fitted kinetics model and that obtained from equation (1) derived directly from experimental data, keeping the effects of temperature and catalyst at mean coded values. The comparison presented in figure 14 shows a good correspondence between the results generated from kinetic model (presented in continuous lines) and that deduced from experimental data plotted in broken lines.

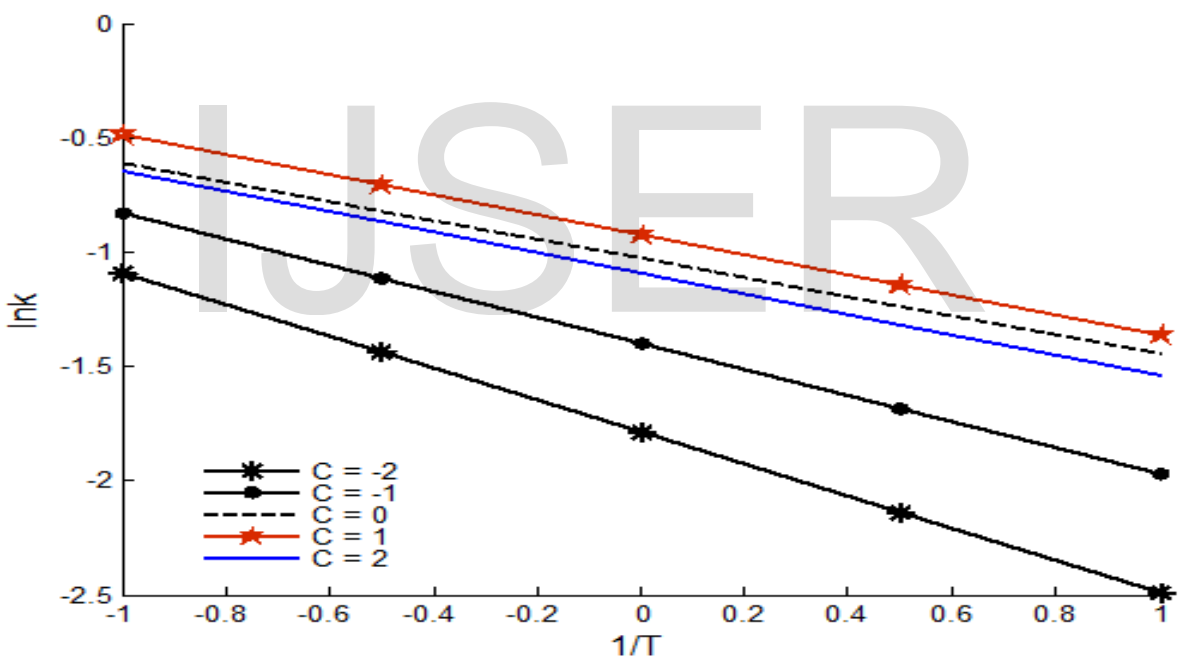


Figure 13: Arrhenius plot for the various conditions of PA/oil ratio

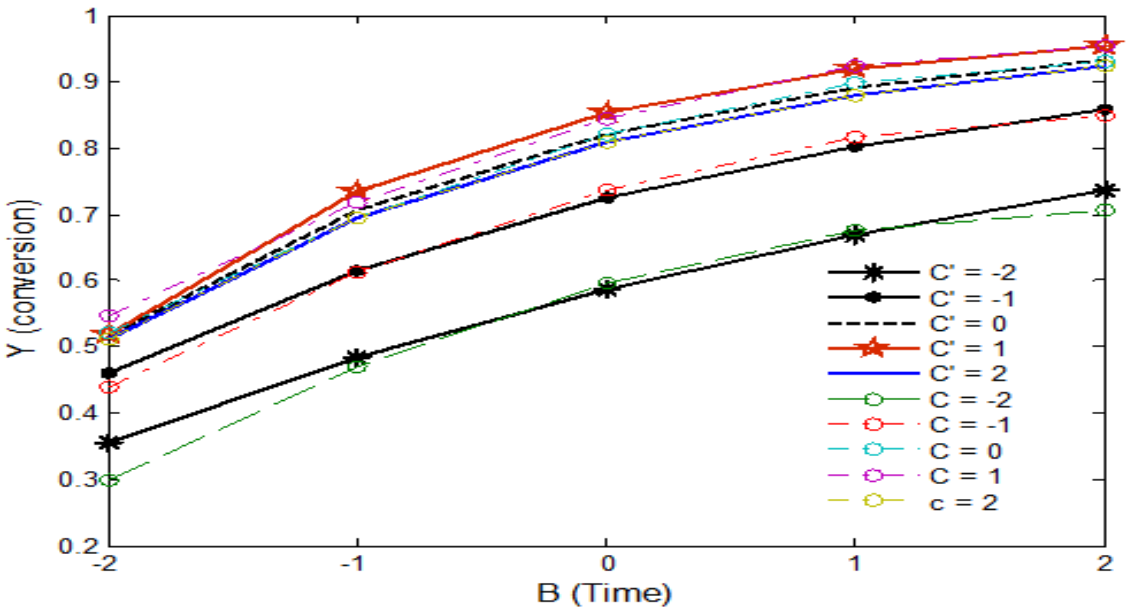


Figure 14: Comparison between alkyd resin conversion derived from experimental data and that predicted by kinetic model

4.0 Conclusion

The kinetics of cottonseed oil modified alkyd resin has been studied within reasonable assumption. The results showed that the forward reaction which favors the production of alkyd resin conform at large to the first order kinetics law while the reverse process is evidently second order. The rate at which the acid value of the reacting mixture drops in the course of reaction is shown to follow linear curves with approximately uniform gradient within the optimum isotherm in the first 120 minutes of poly-esterification process. This trend was subsequently opposed at the later stages of the reactions due to fast degradation of the primary hydroxyl group and the uprising of the secondary hydroxyl group. The values of activation energy further detect a heavy mass transfer resistance during the esterification process. Overall, the present study on the kinetics of cotton oil modified alkyd resin synthesis lead to the following deductions which are important in the batch progress monitoring:

The uncertain kinetic model used led to an on-line estimation of reaction rate parameter and the derivation of the proposed rate model, (ii) The proposed reduced third-order reaction rate model is adequate for predicting the overall acid functional group conversion of the alkyd reactor, (iii) The on-line monitoring of the alkyd reactor based on a viscosity measurement sufficiently guarantees optimal operation of the batch.

5.0 References

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