# Investigation Into The Kinetics Of Palm Kernel Oil Hydrolysis

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## Abstract

The kinetics of producing glycerol and fatty acid from palm kernel oil hydrolysis using only water was studied at various temperatures and pressures. At 1.622 water to oil ratio by weight, a maximum extent of hydrolysis was obtained as 96.85 percent at the temperature of $541^0K$, pressure 500 psi (34 atm) and induction period of 5 hours. Kinetic models are proposed. A Pseudo first order (irreversible) homogeneous reaction model was found to best fit the experimental data obtained. A rate equation for the reaction was developed.

**Keywords:** Hydrolysis, Palm Kernel Oil, Kinetics, Glycerol and Fatty acid.

## 1. Introduction

Kinetics is the quantitative study of the rate of chemical reactions and factors upon which they depend. Various methods have been applied over the years to study reaction kinetics of reacting species. One of the major reactions of economic importance is the reaction that involves splitting of fats and oils to yield glycerol and fatty acid. Existing methods for production of fatty acid are based on chemical and physical methods. The existing industrial process hydrolyses oil to fatty acid and glycerol at the temperature and pressure of $250^0C$ and 50 bars respectively. In this reaction, a 96-99 percent conversion is achieved within two hours (Khor et al., 1985; Noor et al., 2003; Pugazhenthi and Kumar, 2004).

Hydrolysis involves catalyzation of reaction by hydrogen ions. Hydrolytic methods of splitting oil and fat have been discussed by various researchers (Khor et al., 1985; Fadiloglu and Soylemez, 1998; Knezevic et al, 1998 a and b; Rooney and Weatherly, 2001; Knezevic et al., 2004; Ting et al., 2006; Al-zuhair et al., 2007). These methods include the use of (a) Enzyme (b) water (c) water in the presence of an emulsifying agent (d) Alkalis (e) Sulphuric acid (f) Fermentation process.

One of the processes that enhance hydrolysis of oil for substantial overproduction of glycerol commercially is alkali-steered process (Taherzadeh and Adler, 2002; Wang et al., 2001; Walker, 1998). Water-steered process may equally be of great importance. Water can easily be sourced. It can serve as a catalyst and medium from which glycerol could be obtained from oil hydrolysis (Zhuge et al., 2001; Alber et al., 1996).

Studies have shown that some growth and environmental factors influence glycerol production (Alber et al., 1996; Dequin, 2001; Omori et al., 1996; Karasu and Ozbas, 2004; 2005 and 2006;

Remize et al., 2000; Taherzadeh et al., 2002). It has been reported that as temperature increases, the production of glycerol becomes higher (Gardner et al., 1993; Remize et al., 2000). The maximum production of glycerol and corresponding optimum temperature depend on the catalyst used for the hydrolysis (Heard and Fleet, 1998; Remize et al., 2000; Scanes et al., 1998; Wang et al., 2001).

For hydrolysis of fat using water the reaction occurred in a two-phase system, namely: (a) an oil phase containing glyceride, fatty acid, glycerol and water and (b) a water phase containing glycerol and water. The solubility of water in fat phase changes appreciably during hydrolysis. The reaction proceeded stepwise from triglyceride to diglyceride to monoglyceride. Fat splitting approaches completion if large quantity of excess water is used or if one of the products can be removed from the reaction mixture (Jenson et al, 1969; Jeffrey et al, 1961).

Sturm and Fric (1938) developed a correlation for the extent of hydrolysis at equilibrium as:

$$Degree\ of\ hydrolysis\ =\ \frac{3100\ \times\ \%\ water}{31\ \times\ \%water\ +\ saponification\ value\ of\ oil\ (SV)} \quad (1)$$

An empirical relationship was developed by Lascary (1952) for the degree of hydrolysis and glycerol concentration as

$$H^*\ =\ 100 - 0.8G \quad (2)$$

Where, H* is the degree of hydrolysis at equilibrium and G the percent of glycerol in the sweet water. This relationship was proposed as valid for glycerol concentration less than 20 percent.

Serri et al.2008, determine the degree of hydrolysis and rate of hydrolysis of cooking palm oil using C. rugosa lipose. The degree of hydrolysis was determined by titration of the oil phase sample with 0.1m sodium hydroxide (NaoH).

The degree of hydrolysis, X was given as

$$X\% = \frac{(ml\ NaoH\ used)(molarity\ of\ NaoH)\left(\begin{array}{c}average\ molecular\\weight\ of\ fatty\ acid\end{array}\right)}{10\ (weight\ of\ sample)}$$

(3)

The rate of hydrolysis r, was given as

$$r = \frac{S_O}{w}\left(\frac{dx}{dr}\right)$$

Where,

$r = initial\ rate\ of\ hydrolysis\ (mol\ /\ l\ /\ \min)$

$S_O = Initial\ oil\ Concentration\ (g\ /\ l)$

$W = The\ mean\ molecular\ weight\ of\ the\ fatty\ acid.$

$\frac{dx}{dr} = Slope\ of\ \deg ree\ hydrolysis\ versus\ time\ at\ t = 0.$

The kinetic parameters were found using the Michaelis – Menton kinetic equation.        The Michaelis-Menton constant $K_m$ and maximum velocity $V_m$ was evaluated using the double-reciprocal plot (Lineweaver-Burk plot) of reaction rate. The degree of hydrolysis was evaluated to be 97.18%.The stability of enzyme decrease when temperature and PH went beyond enzyme functioning range due to structural deformation (denaturation) of enzyme.
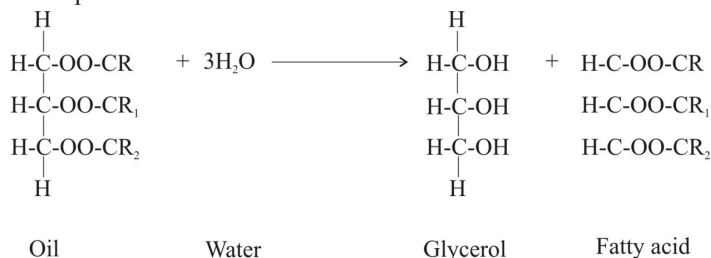
In this study, PKO (palm kernel oil) is considered as a source for the production of glycerol and fatty acid. Water alone is to be used with PKO for the hydrolytic reaction. This study is intended to examine the kinetics of palm kernel oil hydrolysis as a pre-requisite for effective design of a suitable reactor for economic production of glycerol and fatty acid locally.

Glycerol is an economically important alcohol.  Fatty acid is equally important. Both glycerol and fatty acid find applications as raw material in food, beverage, pharmaceutical, tobacco and chemical industries (Zhuge et al., 2001; Viljeon and Heard, 2000; Scanes et al., 1998; Ceccato-Antonini and Sudbery, 2004; Hermansyah et al.,; 2006).

## 2.  Theoretical

### (a) Hydrolytic Reaction

•   The hydrolysis reaction of oil using water is generally represented as

```
   H                                    H
   |                                    |
H-C-OO-CR    + 3H₂O  ──────────▶   H-C-OH    +   H-C-OO-CR
   |                                    |
H-C-OO-CR₁                           H-C-OH        H-C-OO-CR₁
   |                                    |
H-C-OO-CR₂                           H-C-OH        H-C-OO-CR₂
   |                                    |
   H                                    H

  Oil          Water           Glycerol      Fatty acid
```

Where R, $R_1$, $R_2$ are alkyl groups.

•   In the reactor, the reaction mixture (oil and water) is to be thoroughly mixed. Thus, a sample if drawn for analysis would be a uniform mixture of both oil phase and water phase.

•   Acid value (AV) could be used in determining when the oil hydrolysis is complete.

Let us denote the acid value at time zero (0) as $AV_0$

At any given time t the acid value is given as: $AV_t^1$

$$AV_t^1 = \frac{V_K \times N_1 \times M_{oH}}{M_s}\left(\frac{mg\ Sample}{g\ Sample}\right)$$

(4)

Where, $V_K$, $N_1$ and $M_{OH}$ are volume, normality and molecular weight of hydroxide used. $M_S$ is the mass of the sample.

### (b)  Quantitative basis of the reaction

•    The amount of initial number of moles of fatty acid in the oil ($B_{FAO}$) is given as:

$$B_{FAO} = \frac{AV_O \times M_O \times 10^{-3}}{M_{oH}}g - moles$$

(5)

Where, $M_O$ is the initial mass of oil present in the reaction mixture.

•    At any time t the amount of fatty acid $B_{FA}$ is given as

$$B_{FA} = \frac{AV_t \times M_O \times 10^{-3}}{M_{oH}}(g - mole)$$

(6)

$$Where\quad AV_t = \frac{AV_t^1 \times M_R}{M_{oH}}$$

(7)

$M_R$ is the Mass of Oil in the reaction mixture at time (t).

•    At any time t the number of g moles of fatty acid produced ($B_Z$) is given as:

$$B_Z = \frac{M_o \times 10^{-3}}{M_{oH}}(AV_t - AV_O)\quad(g - mole)$$

(8)

Glycerol initially in the oil will decompose by fermentation. Hence at time t = 0 the number of moles of glycerol would ($B_{GLO}$) be zero.

$$B_{GLO} = 0$$

(9)

From stoichiometry, at any time t the amount of glycerol ($B_{GL}$) in the system is given as:

$$B_{GL} = \frac{B_z}{3}(g - moles)$$

(10)

•   At any time t the amount oil remaining in the system ($B_D$) is given as

$$B_D = B_D - \frac{B_Z}{3}(g - moles)$$

(11)

Where ($B_{DO}$) is the number of moles of oil initially present at time t = 0

•   At any time t, the number of moles of water remaining in the mixture ($B_{WT}$)is given by:

$$B_{WT} = B_{WTO} - B_Z \quad (g-moles) \tag{12}$$

The mass of oil phase $M_R$ is given as:

$$M_R = \left( B_{DO} - \frac{B_Z}{3} \right) M_D + \left( B_{WTO} - B_Z \right) X_{WT} M_{WT} +$$

$$\left( B_{FAO} + B_Z \right) X_{FA} M_{FA} + \left( B_{GLO} + B_{GL} \right) X_{GL} M_{GL} \tag{13}$$

Where, $M_D, M_{FA}, M_{GL}$ and $M_{WT}$ are Molecular weights of oil, fatty acid, glycerol and water, respectively.

$X_{FA}, X_{GL},$ and $X_{WT}$ are fractions of fatty acid, glycerol and water in the oil phase, respectively.

Where

$$X_{FA} = \frac{Mass\ of\ fatty\ in\ the\ oil\ phase}{Mass\ of\ fatty\ acid\ in\ the\ mixture} \tag{14}$$

$$X_{GL} = \frac{Mass\ of\ Glycerol\ in\ the\ oil\ phase}{Mass\ of\ Glycerol\ in\ the\ mixture} \tag{15}$$

$$X_{WT} = \frac{Mass\ of\ water\ in\ the\ oil\ phase}{Mass\ of\ water\ in\ the\ mixture} \tag{16}$$

The volume of the oil phase $V_s$ is given as:

$$V_S = \left( B_{DO} - \frac{B_Z}{3} \right) \frac{M_D}{\rho_D} + \left( B_{WTO} - B_Z \right) \frac{X_{WT} M_{WT}}{\rho_{GL}}$$

$$+ \left( B_{FAO} + B_{FA} \right) \frac{M_{FA} X_{FA}}{\rho_{FA}} + \left( B_{GLO} + B_{GL} \right) \frac{X_{GL} M_{GL}}{P_{GL}} \tag{17}$$

Where, $\rho_D, \rho_{FA}, \rho_{GL}$ and $\rho_{WT}$ are the densities of oil, fatty acids, glycerol and water respectively.

(c) **Reaction models:**

In this study, the reaction models proposed for the hydrolysis of oil using water are

(1) first order reaction. (2) second order reversible reaction.

The two models shall be tested and the one that best fits the data would be used with Arrehenius equation to determine the rate equation.

(i) Pseudo First Order Reaction Model

In this model, for a reaction to occur, oil and water form a homogenous phase. The equation for this reaction if irreversible may be written as:

$$\frac{-dC_{D(t)}}{dt} = K_1 C_{D(t)} \tag{18}$$

Where $C_{D(t)}$ is the concentration of the oil in the reaction mixture,

$K_1$ is the first order rate constant.

$$C_{D(t)} = \frac{B_D}{V_S} = \frac{3B_D - B_z}{3V_s} \tag{19}$$

Integrating equation 18 result in

$$In \left[ \frac{C_{DO}}{C_{D(t)}} \right] = K_1 t \tag{20}$$

If a plot of $In \left[ \dfrac{C_{DO}}{C_{D(t)}} \right]$ versus t gives a straight line passing

through the origin, then the data used for the plot fit best this model with $K_1$ being the slope of the graph.

(ii) Second Order Reaction Model

In this model, for a reaction to occur, oil and water form a homogenous phase. The equation for this reaction if irreversible may be written as

$$\frac{-dC_{D(t)}}{dt} = K_2 G_{D(t)}\ C_{WT}\left( t \right) - K_3 C_{FA(t)} C_{GL(t)} \tag{21}$$

Where, $K_2$ and $K_3$ are the rate constants of the forward and

reverse reactions, respectively.

$$C_{WT(t)} = \frac{B_{WT}}{V_S} = \frac{B_{WTO} - B_Z}{V_S} \tag{22}$$

$$C_{GL(t)} = \frac{B_{GL}}{V_S} = \frac{B_Z}{3V_S} \tag{23}$$

$$C_{FA(t)} = \frac{B_{FAO} + B_{FA}}{V_S} \tag{24}$$

$$Equilibrium\ Constant\ \left( K_{eq} \right) = \frac{K_2}{K_3} = \frac{C_{Deq} - C_{WTeq}}{C_{FAeq} C_{GLeq}} \tag{25}$$

Equation 21 may be written in the form:

$$\frac{1}{K_2} \frac{dB_z}{dt} = L + HB_z + NB_z^2 \tag{26}$$

Where,

$$L = \frac{3}{V_S} \left( B_D\ B_{WTO} \right) \tag{27}$$

$$H = \frac{-3}{V_S} \left[ \left( \frac{B_{WTO}}{3} + B_{DO} \right) + \frac{AV_O M_O x10^{-3}}{3M_{oH}\ Keq} \right] \tag{28}$$

$$N = \frac{3}{V_S} \left( \frac{1}{3} - \frac{1}{3Keq} \right) \tag{29}$$

Based on equation 8, the boundary condition for equation 26 is that at time t = 0

$$B_Z = \frac{M_O \times 10^{-3}}{M_{oH}} \left( AV_t - AV_o \right) = 0 \tag{30}$$

Smith (1981) gave the solution of equation 26 with boundary condition as stated in equation 30 as:

$$In\ \frac{\left( 2NB_Z \big/ \left( H - J^{\frac{1}{2}} \right) \right) + 1}{\left( 2NB_Z \big/ \left( H + J^{\frac{1}{2}} \right) \right) + 1} = K_2 J^{\frac{1}{2}} t \tag{31}$$

Where $J = H^2 - 4LN$

If a plot of $In\ \dfrac{\left( 2NB_Z \big/ \left( H - J^{\frac{1}{2}} \right) \right) + 1}{\left( 2NB_Z \big/ \left( H + J^{\frac{1}{2}} \right) \right) + 1}$ versus $t$ gives a straight line

passing through the origin, then the data used for the plot fit best this model; with $J^{1/2}K_2$ equal the slope of the graph.

**(d) Arrhenius Equation**

$$K = K_O \exp\left(-E/RT\right) \tag{33}$$

In $\quad K = InK_O - E/RT \tag{34}$

Where,

| | | |
|---|---|---|
| $K_O$ | = | frequency factor |
| E | = | activation energy |
| R | = | gas constant = 8.314 J/mol°K |
| T | = | temperature °K |

## 3. Materials and methods

### (a) Materials and Equipment

**Fig.1.** *Sketch of a parr pressure batch reactor*
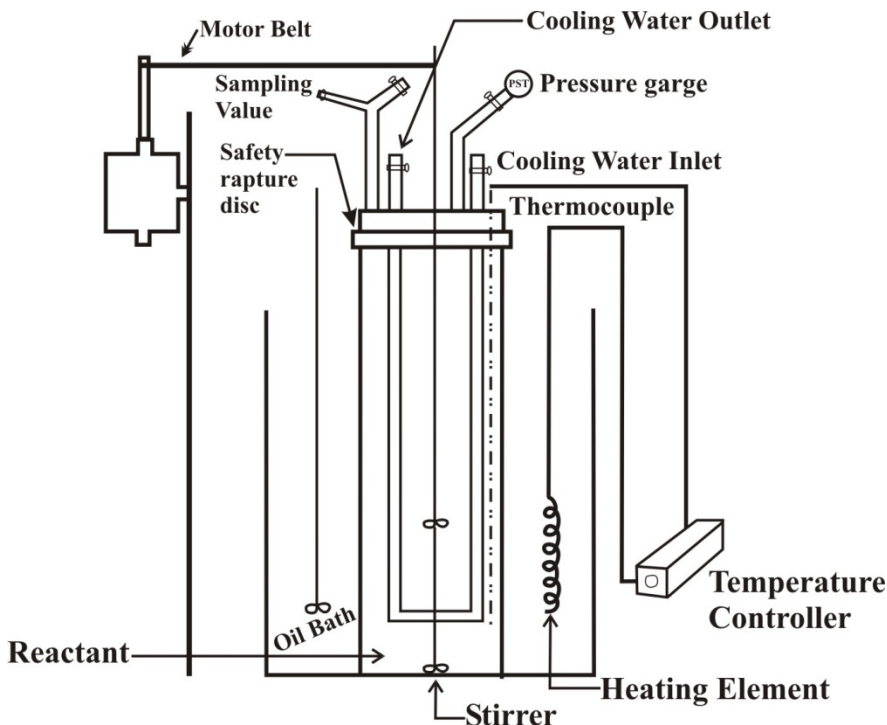


Figure 1 is a parr pressure batch reactor used in the study of palm kernel oil hydrolysis. The reactor is made of high resistance alloy. It has a maximum internal volume of 0.6 litres and can withstand a maximum pressure of 2000psi (136 atm) and temperature 350⁰C (662⁰F). The reactor is fitted with a shaft. The shaft has six-blade turbine type impeller. The shaft is belt-driven by a $1/15$hp constant speed, ball bearing motor. The motor turns the stirrer at a fixed speed of 600rpm. One of the impellers is positioned near the bottom of the vessel. The other impeller is fixed near the base of the vortex. This arrangement enhances any catalyst or suspended solid to remain uniformly distributed throughout the mixture. There would be vigorous gas dispersion into the liquid phase. The reactor has three control valves attached

to the bomb head. One valve is for charging gas into the reactor, the second valve is for withdrawing liquid samples while a run is in progress. The third valve is for releasing gas either during a run or at the conclusion of a run. The gas inlet and liquid sampling valves are both connected to a single dip that extends to the bottom of the reactor. With this arrangement, any incoming gas is always introduced below the surface of the liquid. Two semi-circular split-ring sections are used in clamping the head of the reactor to the bomb cylinder. This ensures maintenance of pressure in the system. The reactor is also fitted with an internal cooling loop through which cold water or compressed air can be passed to remove small quantities of heat from the reactor. This feature can be used to control exothermic reaction or cool reactants at the end of a run. The reactor is heated by immersion in an oil bath. The oil used is "used Engine oil". The heating element of the engine oil is in the bath and is connected to the temperature controller of the reactor. Automatic temperature control is provided by a solid-state potentiometric system operating from a control thermocouple in stainless steel sheath, which is inserted through the bomb head.

The reaction temperature can be read at anytime from a deviation meter mounted on the control panel. Reading can be obtained either by reading the meter or by turning the control knob until the meter reads zero, then reading the dial setting. Switches from the motor and heater are mounted on the panel. The pressure in the system can be read off from a pressure gauge mounted on top of the bomb.

### (b) Procedure

300ml of water and 200ml of palm kernel oil were charged into a reactor. The reactor and its contents were heated to a temperature of 238°C and 380 psi. Samples were collected at intervals of time and analyzed for acid values (AV). When there was little or no change in acid value between subsequent tests, the reaction was stopped. However, samples collected at intervals of time were cooled using ice-chips to slow down the reaction before analysis. The experiment was repeated using the following operating temperature and pressure; 248⁰C and 425 psi; 258⁰C and 450 psi; 268⁰C and 500 psi. For each experiment same ratio of water and oil was used. Models for order of reaction were tested for fitness of the experimental data. Statistical analysis was carried out to estimate Activation energy and frequency factor from Arrhenius equation; hence rate equation determined and its validity tested.

## 4. Result and discussion

Some basic properties of palm Kernel Oil (PKO) relevant to the Kinetics of hydrolysis were analyzed as shown in Table 1.

**Table 1.** *Properties of Palm Kernel Oil Used*

| Density @ 28$^0$C   ($\rho_D$) | 923 kg/m$^3$ |
|---|---|
| Acid value            (AV$_o$) | 51.2 |
| Saponification Value | 248.24 |
| Free glycerol | - |

A high acid value of 51.2 obtained is an indication to expect high fatty acid liberation during hydrolysis as shown in Table 2.

**Table 2.** *Some Parameters of PKO Hydrolysis at 268$^0$C and 500psi, time 5 hours*

| Acid Value | | 240.43 |
|---|---|---|
| Extent of hydrolysis | | 96.85 |
| | Water | 61.86 |
| | PKO | 38.14 |
| % weight of Reactant | | |
| | Fatty acid layer | 44.59 |
| | Sweet water layer | 55.41 |
| % weight of product | | |
| % of Fatty acid in Fatty acid layer | | 95.18 |
| % weight water consumed during hydrolysis | | 34.31 |

This confirms a high value of 95.18 percent free fatty acid obtained at the end of hydrolysis. The acid value variation with time of hydrolysis was monitored at various operating conditions. The extent of hydrolysis was best achieved at 5 hours using temperature 268$^0$C and pressure 500psi (34atm). The reaction limit was observed to be independent of temperature but the rate of hydrolysis increases with temperature. An increase in pressure of the reacting mixture with corresponding temperature increase contributes to increase in rate of reaction. Final acid value usually indicates attainment of maximum extent of hydrolysis. The maximum extent of hydrolysis was observed to be virtually independent of temperature of the oil. It was observed that about 34.31 percent of initial amount of water in the reactor was used up in the reaction. The excess 65.69 percent dissolved the glycerol from the oil – splitting. This glycerol and, water mixture is termed as 'Sweet water'.
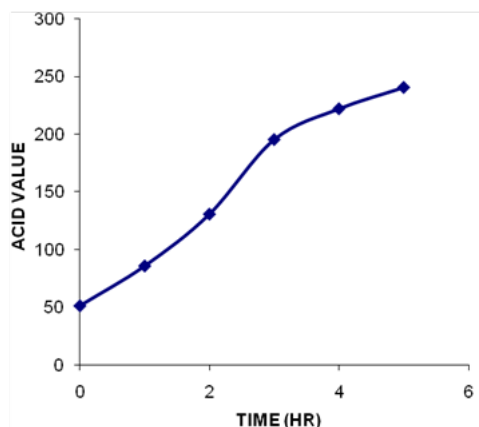
**Fig.2.** *Acid Value Versus time*



Figure 2 shows a gradual increase in acid value from time t = 0 to 2 hours and a rapid increase from 2 to 5 hours. This implies increase in fatty acid and hence rapid increase in glycerol production between time t = 2 to 5 hours. A close observation of this Figure 2 generally shows an initial slow increase then rapid increase before the curve approaches an equilibrium state asymptotically.

The high extent of hydrolysis (96.85%) is in line with Serri et al.2008 observation in hydrolysis of cooking palm oil. Moreover, the experimental data obtained at various operating conditions were computed and plotted as shown in Figure 3 and 4 with respect to the two models proposed and represented by equations 16 and 19.

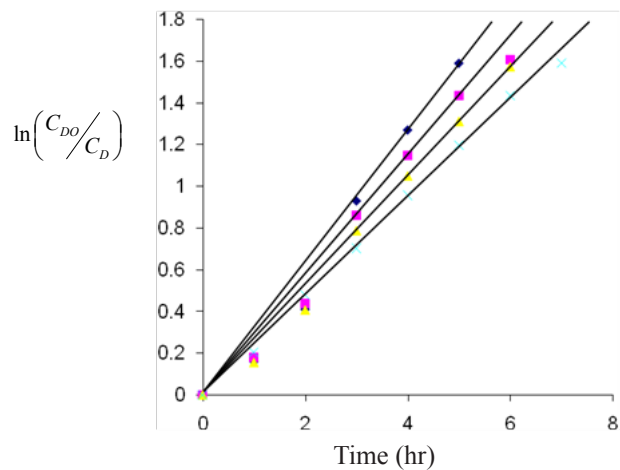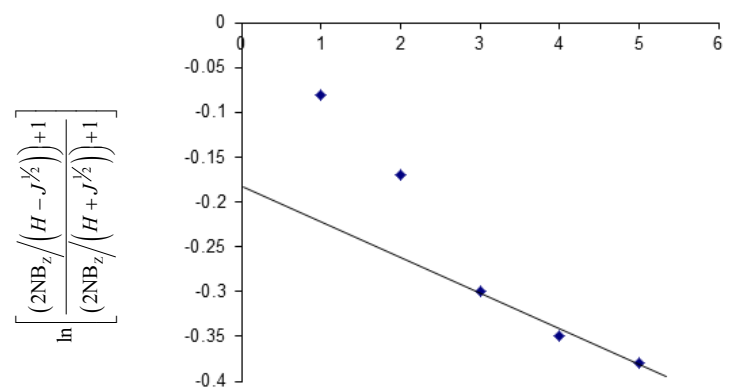**Fig.3.** *ln* $C_{DO}/C_D$ *versus time at various Temperature*



**Fig.4.** *A plot of* $\ln\left[\dfrac{\left(2NB_Z/\left(H-J^{1/2}\right)\right)+1}{\left(2NB_Z/\left(H+J^{1/2}\right)\right)+1}\right]$



The data best fit model one (Pseudo first order irreversible reaction) as evident in Figure 3 and comparable with model two (2$^{nd}$ order irreversible reaction) as Shown in Figure 4. The dependence of rate constant K on temperature for Palm kernel oil is shown in Figure 5.

**Fig.5.** *Arrhenius plot of* ln *k versus* $I/T$ *for model one*
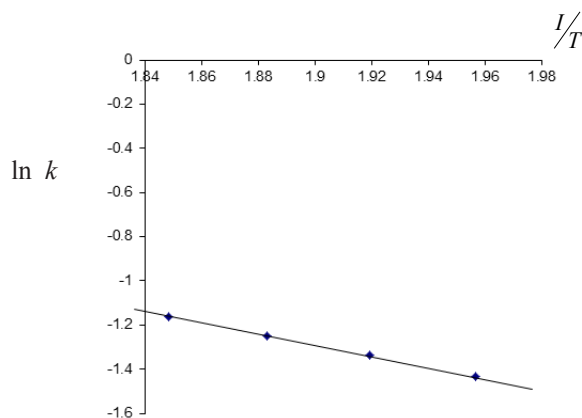


The rate constant was obtained as

$$K = 29.69 \exp.\left(\frac{-2463.88}{T}\right) hr^{-1}$$

From equation 18, the rate equation is given as:

$$\frac{-dC_D}{dt} = 29.69 \exp.\left(\frac{-2463.88}{T}\right)C_D$$

The validity of the above equation was tested with values shown in Table 3.

**Table 3.** *Predicted and Experimental Values for Glycerol yield during PKO Hydrolysis ( Operating Conditions: Temperature 541K Pressure 500psi. )*

| Experimental Values (Using Acid Value) | | Predicted Values Using Rate Equation | | |
|---|---|---|---|---|
| $C_D$ | $B_{GL}$ (Glycerol gmoles) | $C_D$ | $B_{GL}$ (Glycerol gmoles) | Time (hr) |
| 0.522 | 0.000 | 0.522 | 0.000 | 0 |
| 0.446 | 0.0380 | 0.382 | 0.0700 | 1 |
| 0.347 | 0.0875 | 0.280 | 0.1210 | 2 |
| 0.205 | 0.1585 | 0.204 | 0.1590 | 3 |
| 0.147 | 0.1875 | 0.150 | 0.1860 | 4 |
| 0.106 | 0.2080 | 0.190 | 0.2065 | 5 |

From statistical analysis, this equation is reasonably reliable with standard error 3.76%.

## 5. Conclusion

An achievable degree of hydrolysis 96.85% was obtained at temperature 268⁰C, water to oil ratio 1.622 by weight with induction period 5 hours.

The induction period of 5 hours could be reduced if water and oil are raised to 268⁰C and brought into contact in a reactor at water to oil ratio of 1.622 by weight.

Water to oil ratio seems to affect the limit of hydrolysis, hence glycerol production

The rate of reaction for the production of glycerol was (a) favorable at temperature 268⁰C and pressure 500psi (34atm) and water to oil ratio 1.622 by weight (b) found to be pseudo first order homogenous (irreversible) reaction.

The rate of production of glycerol was found to follow the empirical equation.

$$\frac{-dC_D}{dt} = 29.69 \exp.\left(\frac{-2463.88}{T}\right)C_D$$

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## 7. Constants

(i) List of constant for Palm Kernel oil.

$$\rho_{FA} = 860.00\,kg/m^3$$
$$M_{FA} = 217.80$$
$$AV_0 = 51.20$$
$$AV_{eq} = 241.20$$
$$M_D = 709.00$$
$$\rho_{GL} = 1256\,kg/m^3$$

(ii) Other Constant (Rose and Freshwater, 1962; Cock and Rode, 1966; Perry and Chilton, 1973)

$$\rho_{WT} = 1000\,kg/m^3$$
$$M_{WT} = 18.00$$
$$M_{GL} = 92.10$$
$$X_{FA} = 1.00$$
$$X_{WT} = 0.10$$
$$X_{GL} = 0.00$$