Journal of Oil Palm Research Vol. 18 December 2006 p. 278-287

AUTOCATALYTIC HYDROLYSIS AND AUTOXIDATION OF CRUDE PALM OIL UNDER VARIOUS CONSTANT HUMIDITIES

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ABSTRACT

The kinetics of autocatalytic hydrolysis of crude palm oil was studied at moisture below solubility using the isopiestic method, in which the oil was exposed to a volume of sulphuric acid at a certain concentration in a closed system and stored at 55°C. Different humidities were created by using different concentrations of sulphuric acid, thereby effecting different activities of water in the oil. The reaction rate constants of crude palm oil with different initial free fatty acid contents and initial moisture contents stored under the constant humidities created were determined and studied. The oxidation of the oil samples under these different constant humidities was also studied.

Autocatalytic hydrolysis of crude palm oil, or similar glyceridic oil, of a low free fatty acid content, and under constant water activity, follows a zero-order reaction. The rate of reaction is a function of the initial free fatty acid content. The reaction rate constant is a direct function of the initial free fatty acid content and water activity or moisture content. Water activity of >0.50 is desirable for a lower rate of autoxidation of the oil in storage.

Keywords: FFA, moisture, kinetics, hydrolysis, oxidation.

Date received: 13 April 2006; **Sent for revision:** 8 May 2006; **Received in final form:** 6 July 2006; **Accepted:** 1 August 2006.

INTRODUCTION

Loncin (1952) studied the autocatalytic hydrolysis of crude palm oil at saturated moisture in the presence of excess water at 60°C-80°C. Under the condition, and at low free fatty acid (FFA) levels of less than 10%, the concentrations of esters and water can be regarded as constant. The rate of reaction then simplifies to the zero-order equation, df/dt = constant, where *f* is the free fatty acid content, and *t* is the time in days. However, Loncin could not confirm the expression experimentally. He hypothesized instead that the rate of autocatalytic hydrolysis for a low FFA oil is proportional to the level of FFA and can be represented by the first-order equation, df/dt = kf, where *k* is the reaction rate constant (Loncin, 1956; Loncin and Jacobsberg, 1965). On integration the following equation is obtained,

$$2.303\ (\log f - \log f_o) = k\ t \qquad (1)$$

where f_o is the initial FFA content of the crude palm oil. The reaction is unimolecular according to Loncin (1952; 1956). He also stated, although without supporting data, that the reaction becomes second order and bimolecular when the concentration of water is below saturation. Accordingly, he represented the reaction rate by df/dt = kf[H_2O].

Jacobsberg (1974) again stated that fatty acid chemical hydrolysis conforms up to 10% FFA to the kinetics of a reaction of order zero, and presented the following integrated equation that takes into

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consideration the effect of moisture below oil solubility:

$$2.303 (\log f - \log f_o) a_\omega = k t \quad \text{.....................(2)}$$

where a_ω is the water activity defined as the ratio of the moisture in the oil over the solubility of water in the oil of a certain FFA content and temperature, or the ratio of the vapour pressure (P) of the dissolved water in the oil over the vapour pressure (P_o) of free water (Loncin 1965).

Recent work on autocatalytic hydrolysis and autoxidation of crude palm oil has been reviewed (Chong, 1995). However, there has been very little published work on autocatalytic hydrolysis of crude palm oil at moisture level below saturation when $a_\omega < 1$. This study attempts to look at the reaction rate of autocatalytic hydrolysis of crude palm oil at moisture levels below solubility at 55°C where the oil is liquid. Samples of crude palm oil, with initial FFA content of 1.0% to 6.5%, were allowed to undergo autocatalytic hydrolysis under a range of constant water activities. This constancy of water activity was effected by exposing the samples to a range of constant humidified atmospheres created using different concentrations of sulphuric acid in a closed system (Hilder, 1968). The rate of autoxidation of the oil samples under these humidity conditions was also studied.

EXPERIMENTAL

Materials

Crude palm oil. Eight crude palm oil samples with the following initial FFA contents were used: 2.46% and 2.64% (average 2.55%), 3.33% and 3.61% (average 3.47%), 4.44% and 4.71% (average 4.55%), and 5.56% and 6.27% (average 5.92%). An oil with 1.07% FFA was mechanically expressed from sterilized oil palm fruits in the laboratory.

Glycerol tri-oleate. A sample of glycerol tri-oleate with FFA content of 0.36% (as oleic acid) was obtained commercially. This was used to simulate a palm oil with very low FFA.

Hydrolysis apparatus. Thirty-five sets of hydrolysis apparatus, each consisting of two quickfit conical flasks (100 ml) inter-connected by an inverted U-tube having quickfit cone-joint at both ends, were used.

Oven. The oven temperature was monitored using a thermometer placed vertically in the centre. The oven was set at 55°C +/- 1°C.

Methods

Hydrolysis procedure. Each palm oil sample was subject to seven different constant humidity conditions. Under each condition, five sets of hydrolysis apparatus were used to monitor the progress of the autocatalytic hydrolysis. The seven constant humidity conditions were created using sulphuric acid of concentrations (volume/volume), 0%, 10%, 19%, 23%, 30%, 45%, and 60%. For each set of apparatus, 50 g sulphuric acid were put into a conical flask and 50 g of the palm oil sample in the other flask. The two conical flasks were then stoppered together with the quickfit joints of an inverted U-tube without the use of clips. The five sets of apparatus for each treatment were placed randomly in rows in the oven.

Every seven days, for 35 days, one set of apparatus from each treatment was removed from the oven. An oil sample (5 g) was taken for determination of FFA, and another (0.1-0.2 g) for moisture determination using a Metrohm Karl Fisher automatic titrator. Oil samples were also taken for the measurement of oxidative parameters of UV-absorption at 269 nm and carotene value at 446 nm to compute the DOBI (Deterioration of Bleachability Index) (Swoboda, 1981; 1982).

Data analysis. Regression analysis, curve fitting of the data and the production of charts and tables were carried out using Microsoft Excel 97 software. In the chart, the R^2 values are presented together with their degrees of freedom, df, to indicate the significance level of the correlations.

RESULTS

Figure 1 shows the plots of the determined individual equilibrium moisture values against the determined FFA values for each of the humidity conditions from all the sets of hydrolysis data. The points considered spurious were omitted. The accuracy of the Karl Fisher moisture values became poorer with increasing moisture level. Most of the discarded points were from the saturated water set of data. The scattered saturated moisture values were also due to the presence of water droplets during sampling making the procedure difficult.

Linear regression analysis on the seven sets of data gave seven linear equations relating the moisture level of the crude palm oil with its FFA content at the various humidities. All the correlations achieved had $R^2 > 0.640$, df = 37 to 47, except for the two sets involving very low humidities where $R^2 < 0.484$. The ratio of the slope of each linear plot over

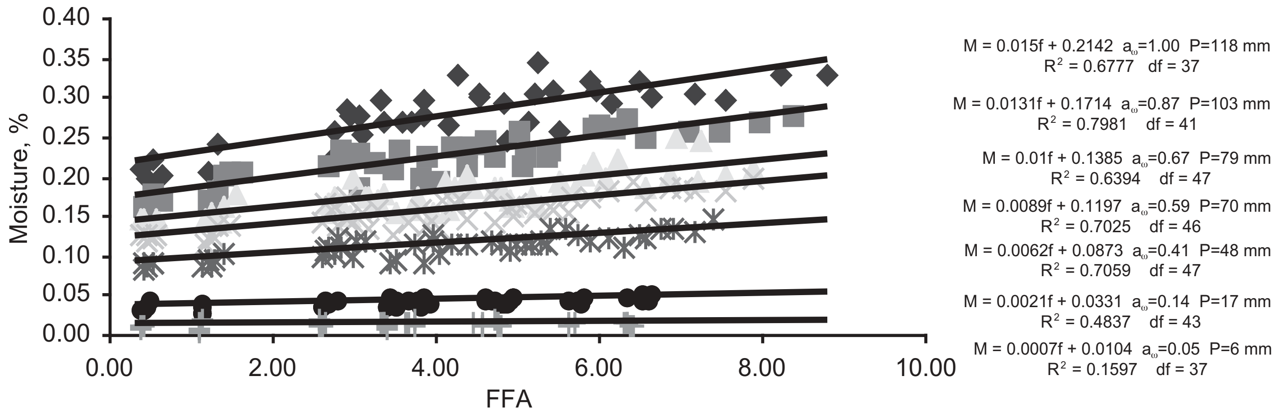

Figure 1. Relationship between moisture of crude palm oil and FFA content.

the slope for crude palm oil with saturated moisture gave the water activity, a_ω, as defined by Loncin (1965). The a_ω value for each humidity condition is shown beside the linear plots. Taking the saturated vapour pressure, P_o, of water at 55°C to be 118 mm Hg, the water vapour pressures, *P,* for the other humidity conditions, as shown in *Figure 1,* were calculated using the equation, $a_\omega = P/P_o$.

It could be shown by the linear regressions that the slopes (S) of the seven linear equations were related to water activity by the Equation $S = 0.015a_\omega$ ($R^2 = 0.9999$, df = 5), and that the intercepts (I) were related by the Equation $I = 0.205a_\omega + 0.002$ ($R^2 = 0.995$, df = 5). From these functions, a general relationship between M, moisture content, FFA & a_ω was obtained as follows:

$$M = (0.015f + 0.205)a_\omega + 0.002$$

By ignoring the insignificant factor of 0.002, the equation simplified to

$$M = (0.015f + 0.205)a_\omega \quad \text{………………………..…..(3)}$$

Rate of Autocatalytic Hydrolysis under Constant Humidity

For each crude palm oil of a particular initial FFA content, the determined FFA values were plotted against time in days for each humidity treatment, or at constant a_ω. Each sample therefore had seven relationships corresponding to the 7 a_ω's. *Figure 2* shows a set of typical positive linear regressions of FFA *vs. t* for a crude palm oil with f_o of 3.61%. The slope of each plot is therefore $df/dt = k$, a constant, which is the reaction rate constant for a zero-order reaction having the unit % per day. The coefficients of correlation, R^2, were 0.984 - 0.993, df = 4, except for the two relationships at low water activities of 0.14 and 0.05. This trend was generally observed for the other sets of *k* values for the other crude palm oil samples.

Figure 3 shows the linear regressions of all the *k* values against the initial FFA values for each a_ω. The mean FFA and *k* values were used for the four sets of data derived from the four duplicated sets of palm oil samples (mean FFA range: 2.5% - 6.0%) as

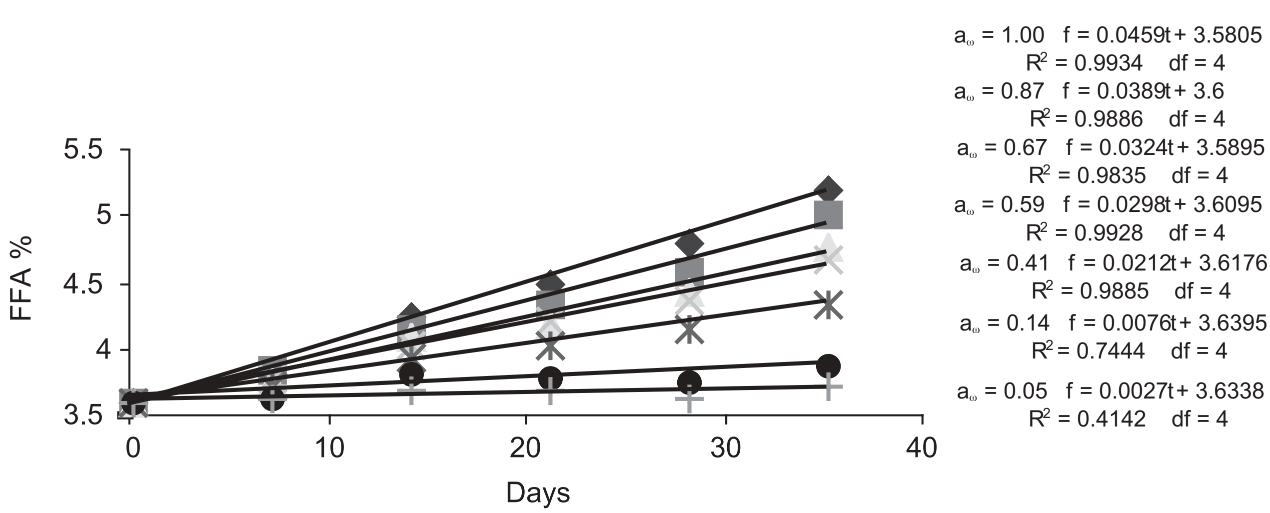

Figure 2. Determentation of zero-order rate constant of autocatalytic hydrolysis of crude palm oil with initial FFA of 3.61% at constant water activity.

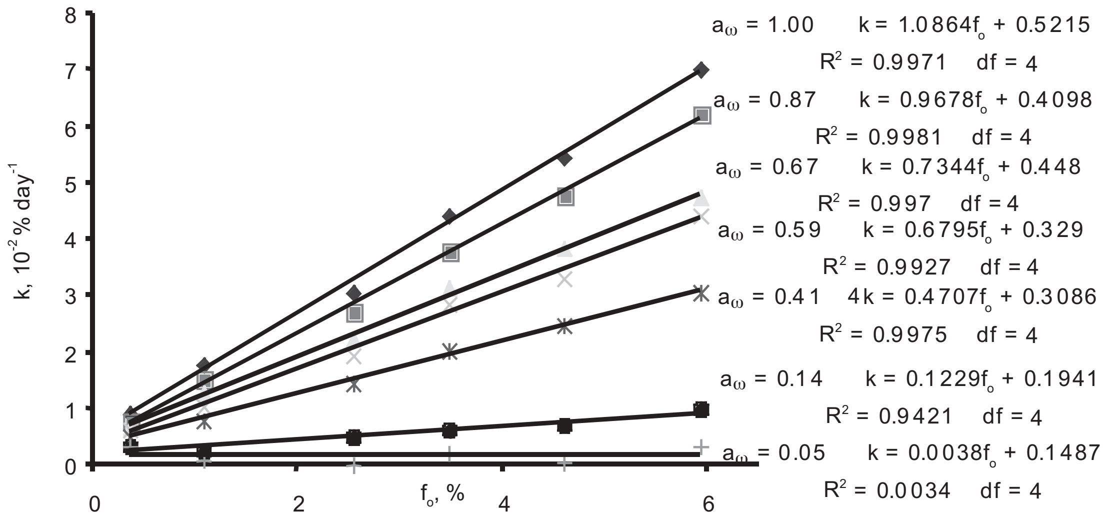

Figure 3. Effect of initial FFA on the rate constant of autocatalytic hydrolysis of crude palm oil at various constant water activity.

described in the Experimental section. The correlation coefficients, R^2, were 0.942 – 0.998, df = 4, for $a_\omega > 0.05$. A linear rate of increase in the rate of hydrolysis with the initial FFA at constant water activity was observed. At $a_\omega = 0.05$, there was insignificant effect of initial FFA on the rate of reaction.

Figure 4 shows linear regression plots of *k* values against a_ω values for crude palm oil samples with various initial FFA contents. The linear regressions were computed through the zero intercept. The correlation coefficients, R^2, were > 0.990, df = 5, except for the extremely low f_o set of data, where $R^2 = 0.612$. The linear increase in hydrolysis rate with increasing water activity increased with the initial FFA content.

Figure 5 shows the 3-dimensional surface of k *vs.* f_o and a_ω.

Autocatalytic Hydrolysis under Constant Moisture Content

When the *k* values were plotted against the initial equilibrium moisture contents (*M*) for each crude palm oil of a certain FFA, the plots in *Figure 6* were obtained. The initial equilibrium moisture contents of the crude palm oil under the seven humidities were derived by reading the values against the initial FFA of the crude palm oil samples in *Figure 1*. The mean *k* and moisture values from the four duplicated sets of data were used. The rate constant of autocatalytic hydrolysis of crude palm oil increased in a linear manner with the initial moisture content. The linear regression equations were computed through the zero intercept. The correlation coefficients, R^2, were all > 0.987, df = 5, except for the set with extremely low f_o. This relationship is

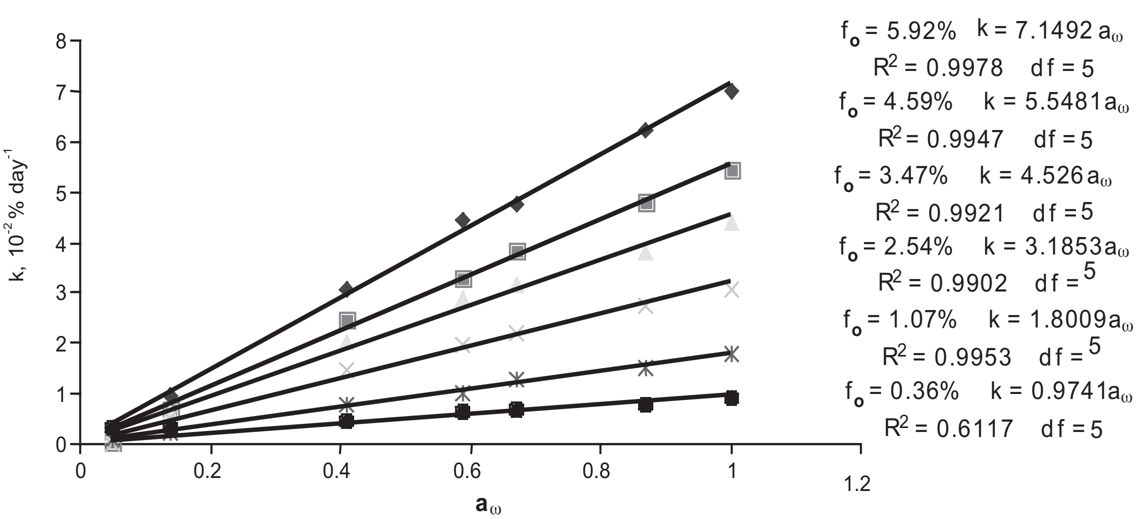

Figure 4. Effect of water activity on the reaction rate constant of autocatalytic hydrolysis of crude palm oil at various constant initial FFA.

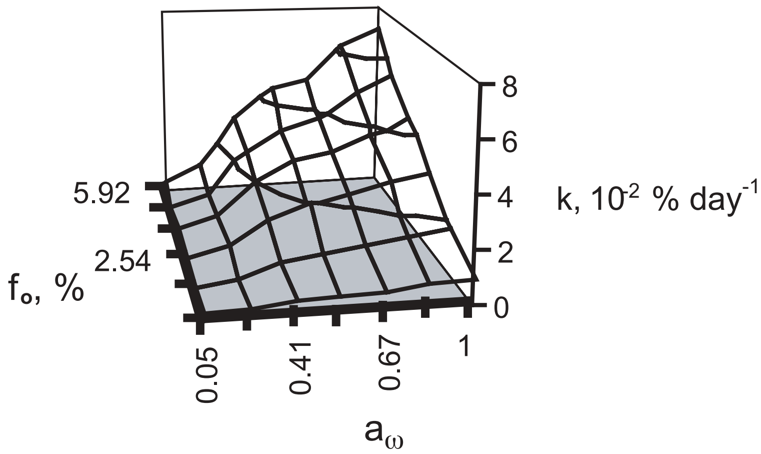

Figure 5. The 3-D surface of reaction rate constant k *of autocatalyic hydrolysis of crude palm oil against initial FFA and* a_ω.

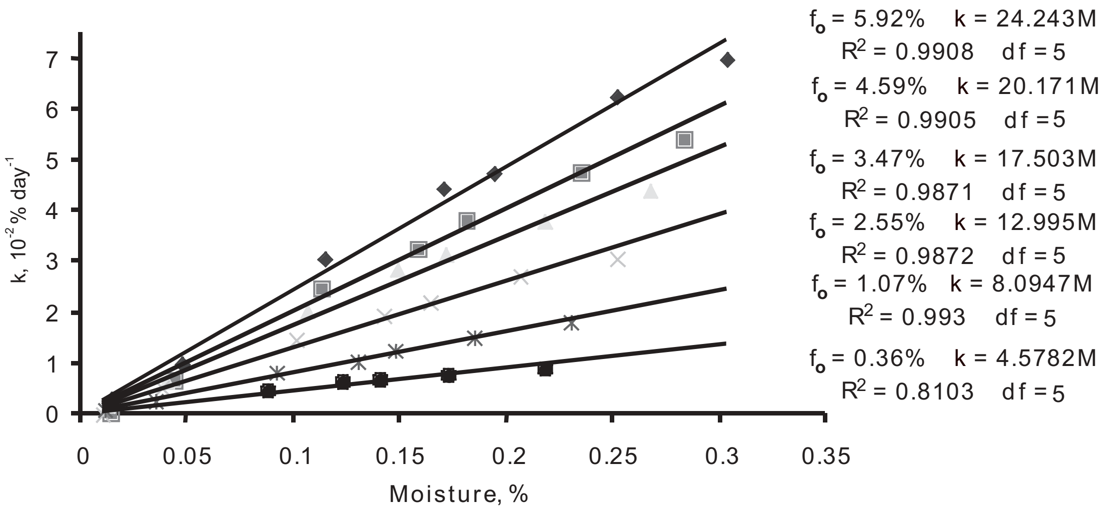

Figure 6. Effect of initial moisture on the rate constant of autocatalytic hydrolysis of crude palm oil at various initial FFA.

expected from the linear relationship between M and a_ω in Equation 3.

The k-values for the six crude palm oil samples at 0.05%, 0.10%, 0.15%, 0.20% and 0.25% initial equilibrium moisture contents were derived from the linear equations in *Figure 6* and plotted against the initial FFA values as shown in *Figure 7*. The relationship of *k* with f_o, at constant moisture content could be expressed by a linear equation as in the case with constant a_ω. Five linear equations were well fitted to the sets of points, with $R^2 > 0.979$, df = 4 except for the series with M = 0.25% where df = 2.

Figure 8 shows the 3-dimensional plot of *k vs.* f_o *vs.* moisture. It must be noted that the interconnecting lines relating to the non-existing points for f_o at 0.36 and 1.07% (*Figure 7*) on the line for 0.25% M should be ignored.

Figure 9 shows the DOBI deterioration of crude palm oil samples with various FFA contents (1.1% – 6.3%) under the range of humidities studied, over storage of five weeks at 55°C. Linear regression analysis of each set of data provided the rates of DOBI deterioration for the samples as shown in *Table 1*. The correlation coefficients, R^2, were in the 0.924 – 0.990 range, df = 4, for all the series, except for the set with 1.1% FFA, where R^2 were 0.843 – 0.948, df = 4. *Table 2* shows the preferred moisture level for each sample for slower autoxidation during storage.

DISCUSSION

The FFA content in commercial crude palm oil never exceeds 10%. Therefore, autocatalytic hydrolysis essentially involves the splitting of triglycerides to diglycerides and fatty acids. The rate of hydrolysis is independent of the fatty acid chain length or position on the glycerol molecule (Loncin, 1952).

Figure 2 shows that the rate of autocatalytic hydrolysis, under constant water activity, follows a zero-order reaction for crude palm oil, with low

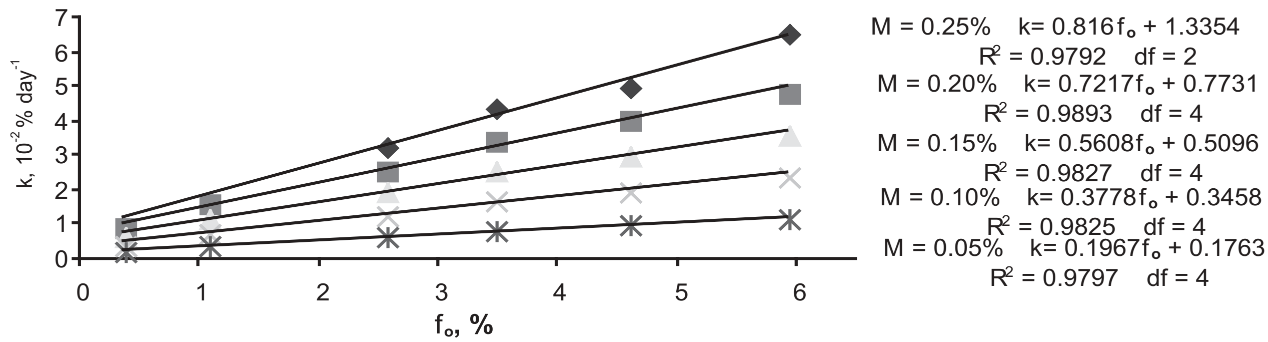

Figure 7. Effect of initial FFA on the rate constant of autocatalytic hydrolysis of crude palm oil at constant initial moisture content.

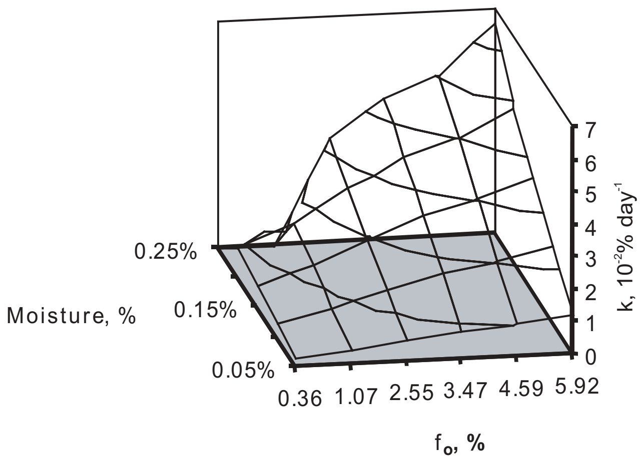

Figure 8. The 3-D surface of reaction rate constant against initial FFA and moisture content.

initial FFA of less than 10%, where df/dt = k, the reaction rate constant having a unit of 10^{-2} % day^{-1}.

In acid catalysed ester hyrolysis, the rate of acid hydrolysis is proportional to the hydrogen-ion concentration (ignoring salt effects and activities), ester and water concentrations in the system (Jellinek, 1952):

$$- dA/dt = k[H_2O] [H^+] [A]$$

where *A* is the ester concentration.

In the present system under study, [*A*] was present in great excess and should be regarded as constant. The small effective water concentration, expressed as constant water activity, remained constant. As the hydrolysis progressed, FFA increased with moisture in the crude palm oil as expressed in Equation 3. The increase in moisture would be expected to be associated with the increases in the polar -OH and -COOH functional groups. However, the maximum increase in moisture for most cases was much less than 10% of the initial moisture content in the oil (refer *Figure 1*). The water concentration therefore remained effectively constant.

For the reaction to be zero-order, [H^+] must be constant. In the acid hydrolysis mechanism, no hydrogen ions are used up. The initial FFA content of the crude palm oil determines the hydrogen ion concentration in the reaction system under study. As the hydrolysis progresses, and FFA increases, the moisture in the system also increases proportionately at constant a_ω, as given by Equation 3. Therefore, the soluble acid concentration, Ca, of the weakly soluble organic free fatty acids in the moisture remains approximately constant. Since $[H^+] = [KaCa]^{-2}$, where *Ka* is the dissociation constant with a very small value about 10^{-4} to 10^{-5} for a weak organic acid, the hydrogen-ion concentration remains constant throughout the reaction. The first-order reaction of df/dt = kf, as proposed by Loncin, is therefore not observed. The rate of autocatalytic hydrolysis is thus determined by the constant hydrogen-ion concentration set by the initial FFA content of the crude palm oil.

The practical implication, as known, is the production of a crude palm oil with low FFA to minimize the rate of subsequent increase in FFA through autocatalytic hydrolysis during storage. The humidity and the initial moisture content are also important factors affecting the rate of FFA increase.

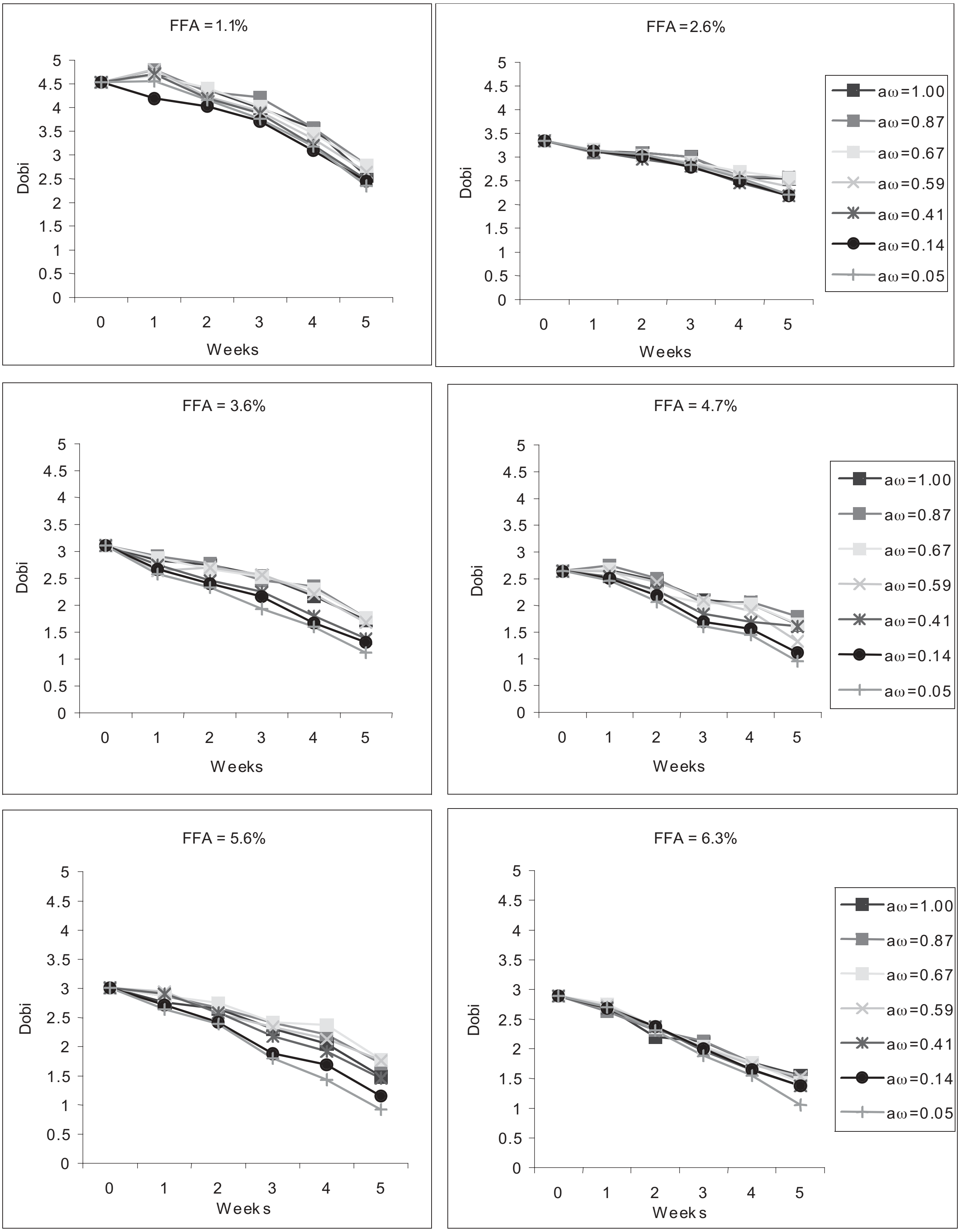

Figure 9. Rate of deterioration of DOBI of crude palm oil of various FFA stored at different humidities.

TABLE 1. RATE OF DOBI DETERIORATION OF CRUDE PALM OIL OF VARIOUS FFA (DOBI per day)

	FFA, %					
a_ω	**1.1**	**2.6**	**3.6**	**4.7**	**5.6**	**6.3**
1	-0.391	-0.166	-0.261	-0.208	-0.288	-0.273
0.87	-0.357	-0.155	-0.249	-0.193	-0.25	-0.28
0.67	-0.365	-0.156	-0.244	-0.202	-0.228	-0.303
0.59	-0.406	-0.187	-0.245	-0.259	-0.255	-0.289
0.41	-0.43	-0.227	-0.335	-0.233	-0.318	-0.317
0.14	-0.4	-0.227	-0.349	-0.313	-0.369	-0.315
0.05	-0.44	-0.217	-0.38	-0.34	-0.419	-0.372
Iron, ppm	2.58	4.15	6.04	8.32	10.11	17.84
Copper, ppm	0.03	traces	0.04	0.04	0.07	0.09
Phosporus, ppm	3.72	17.5	19.1	26	23.4	27.5
R^2 (df = 4) =	0.843-0.948	..........................0.924	to	0.990	....	

TABLE 2. PREFERRED MOISTURE LEVEL IN CRUDE PALM OIL FOR SLOWER RATE OF OXIDATION DURING STORAGE

CPO FFA, %	*FFA range involved, %	Desired a_ω	Equivalent moisture level, %
1.1	1.1-1.8	>0.6	>0.13-0.14
2.6	2.6-3.8	>0.6	>0.14-0.16
3.6	3.6-5.3	>0.5	>0.13-0.15
4.7	4.7-6.6	>0.6	>0.16-0.17
5.6	5.6-7.1	>0.5	>0.15-0.17
6.3	6.3-8.9	>0.5	>0.15-0.15

Note: *FFA range of the crude palm oil involved in the storage.

A parcel of crude palm oil stored at 55°C in a humid tropical port and exposed to the atmosphere is expected to end up with higher FFA than if stored in a drier temperate environment like Amsterdam. This therefore implies that dehuminification of the air space above the crude palm oil in the tank may be advantageous to reduce the rise in FFA in long storage.

In *Figure 4*, the series of linear regressions can be generalized as $k = Sa_\omega$ at each f_o, where *S* is the slope. When the six S-values are plotted against their corresponding f_o, a linear regression line is obtained where $S = 1.237f_o$, $R^2 = 0.978$, df = 4, when linear regression is computed through the zero intercept, or $S = (1.105f_o + 0.559)$, $R^2 = 0.998$, when the zero intercept is omitted. In order to obtain a simple general equation, the latter is ignored and the following obtained:

$k = 1.237\, f_o\, a_\omega$ .... (4)

The reaction rate constant is a direct function of the initial FFA and water activity. At saturated moisture, where $a_\omega = 1.00$, the equation, $k = 1.237f_o$, is obtained. Similarly, using the data in *Figure 6*, the following

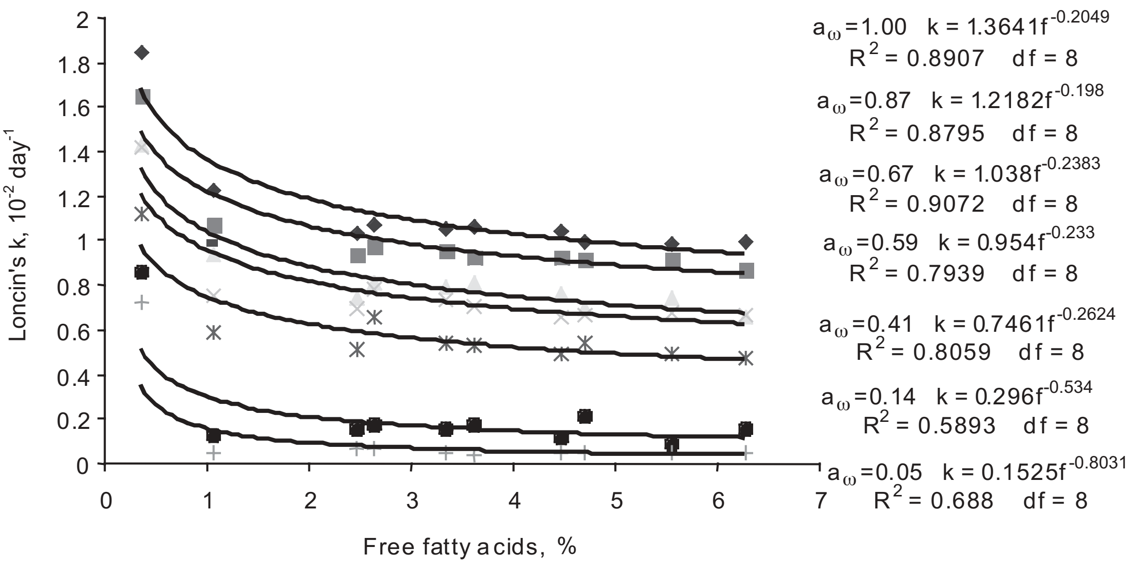

Figure 10. Effects of free fatty acids and water activity on the rate of auto-catalytic hydrolysis of crude palm oil according to Loncin's equation.

equations can be obtained relating k to f_o and M: $k = (3.523f_o + 4.052)M$, or in simpler form, $k = 4.481 f_o M$.

If the present data are fitted into Loncin's Equation 1, a series of relationships between Loncin's k - values with f_o and a_ω are obtained as shown in *Figure 10*. The k-values tend to infinity as f_o tends to zero, and zero as f_o tends to 100%. Loncin's k constant depicts the rate of FFA increase with respect to the initial FFA content of the crude palm oil. This trend may therefore explain Loncin's statement (1952), given without much detail, that at more than 35% FFA, and moisture below solubility, the hydrolysis reaction is strongly retarded and that the retardation is satisfactorily explained by the inverse reaction of free hydroxyl groups.

It has also been stated that spontaneous autocatalytic hydrolysis of fats and oils is not possible when the activity of water falls below 0.5 (Loncin, 1965), or ceases when the moisture content is brought down below 0.1% (Loncin and Jacobsberg, 1965; Jacobsberg, 1969; 1974). The other conditions are not well specified. Current observations show that the rate constant at 55°C is still substantial and detectable when $a_\omega \leq 0.5$ (*Figure 3*), or moisture ≤ 0.1% (*Figure 7*), in commercial crude palm oil with 2.0% – 6.5% FFA. It is only at around $a_\omega = 0.05$, or M < 0.05%, that autocatalytic hydrolysis becomes insignificant. However, at ambient tropical temperature of about 30°C, when the oil is partially crystalline, the rate of reaction for the olein fraction would be less than a quarter that at 55°C, according to the Arrhenius Equation (Loncin, 1952; Desassis, 1957).

Autoxidation

From *Table 1*, it can be seen that as a_ω decreases the rate of DOBI deterioration generally increases towards a low a_ω value of 0.05. *Table 2* shows the minimum desirable humidity to be > 50% at 55°C , or $a_\omega > 0.5$ (Jacosberg 1974), for storage of commercial crude palm oil with normal FFA of 2.0%-6.0%, which is translatable to a minimum desirable moisture content of generally not less than 0.1%. There appears to be a direct positive correlation between the minimum preferred moisture and FFA (*Table 2*), and also between trace metals and FFA (*Table 1*). This could be an indication of the need for water of co-ordination to reduce the catalytic effect of these trace metals (Chong, 1995). However, the rate of DOBI deterioration appears not to be a function of the FFA content nor that of the pro-oxidants of iron and copper in the oil. But it is significant that the initial DOBI of the crude palm oil is inversely related to the initial FFA (*Figure 9*).

CONCLUSION

Autocatalytic hydrolysis of crude palm oil, and other triglyceridic oils of similar fatty acid chain lengths, with an initial FFA content below 10%, follows a zero-order reaction at constant water activity. The reaction rate is a direct function of the initial FFA content and water activity, or moisture content. A simple equation, $k = 1.237f_o a_\omega$, describes the reaction at 55°C.

The current set of data did not show an optimum moisture level for hydrolytic and oxidative protective effect of crude palm oil (Chong, 1995). However, the current observations confirm that for any protective effect against oxidation, the water activity should be > 0.5, or moisture > 0.1% (*Table 2*).

ACKNOWLEDGEMENT

This research was carried out when the authors were attached to Guthrie Research Chemara, Seremban, Malaysia. The authors thank Kumpulan Guthrie Berhad for the publication of this paper, Tee Kim Ming for technical assistance, Michael K H Goh and Ahmad Alwi, former statisticians of Guthrie Research Chemara, for useful comments on the statistics presented.

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