

Mongana Basics: Part 13 - De-hydration and Re-hydration of Oil**

N Ravi Menon*

Experiments on the spontaneous hydrolysis of palm oil have shown that the reaction is of the type of the common hydrolysis; the so-called catalyzed monomolecular hydrolysis; that is, the formula of the instantaneous speed of reaction does not include a factor linked to the moisture concentration so long as the latter is close to saturation.

However, in practice, if the moisture content is appreciably below the solubility limit, the speed of reaction of the hydrolysis is considerably reduced. Practically, when moisture content reaches the level of 0.1% and if there is no moisture available to compensate for the water utilized in the hydrolysis, it may be considered that the acidification process is almost completely stopped. This is due on one hand to the fact that for moisture contents around 0.1%, the hydrolysis proceeds at a velocity markedly lower than that prevailing at or close to saturation level and, on the other hand, to the fact that any tendency to hydrolysis entails a depletion of moisture and consequently a slower reaction speed.

The problem of oil storage is therefore primarily one of drying and secondly, one of preventing the absorption of atmospheric moisture.

* Malaysian Palm Oil Board,
P. O. Box 10620, 50720 Kuala Lumpur, Malaysia.

** Continued from p. 23 of Palm Oil Engineering Bulletin
Issue No. 87.

The study which has been undertaken consists of the following:

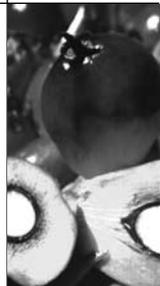
- study of the solubility of water in palm oil;
- determination of the vapour pressure of the dissolved water;
- drying through dry air bubbling;
- industrial drying of oil or dehydration;
- hygroscopic characteristics of the oil that is the rate of moisture absorption in humid surroundings; and
- speed of moisture absorption under industrial conditions, *i.e.* re-hydration.

These points are examined in detail below.

Solubility of Water in Oil

This has been determined in relation to temperature, free fatty acid (FFA) content and free hydroxyl radicals. The determination is carried out by centrifugation of the oil to which has first been added an excess of water. A special container is used. The water content of oil is determined after prolonged centrifugation. In fact, the solubility corresponds to the asymptote of the dissolved water contents recorded after multiple centrifugations.

The determination of water in oil is carried out using acetyl chloride (Kaufman and Funeks). The solubility curve of a few samples of oil is given in Figure 1. The solubility increases with increasing FFA



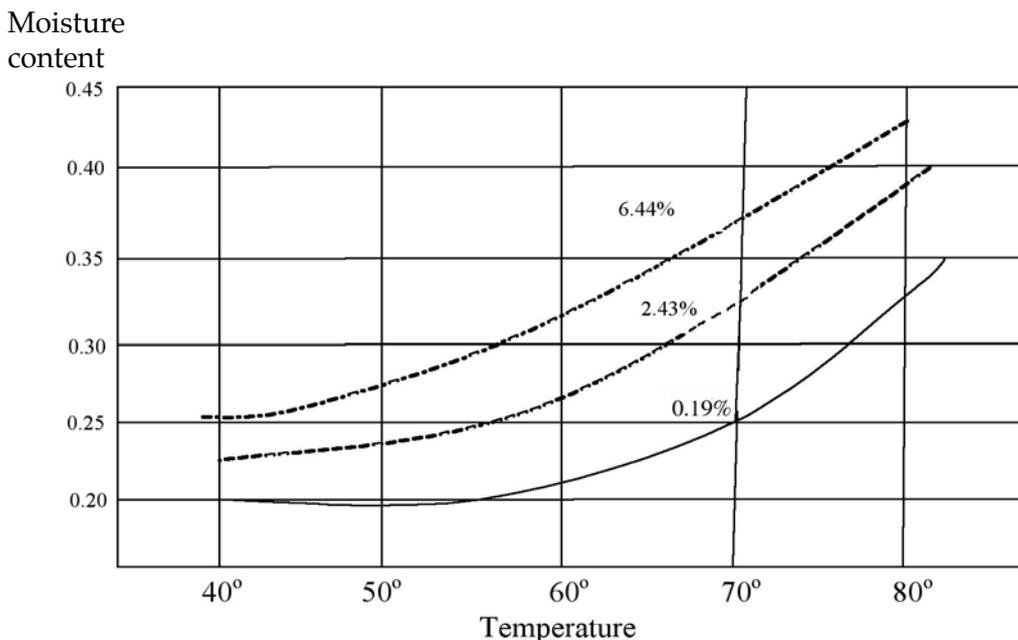
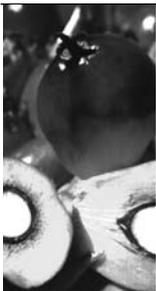


Figure 1. Solubility of water in palm oil vs. temperature and initial FFA content.

content and with higher temperature. Comparative tests on refined oil to which fatty acid has been added and on naturally acidified oil, that is possessing a high hydroxyl value, show that the free OH radicals play a part in the solubility of water in oil but a lesser one than that of temperature or FFA.

The determination of the solubility of water in oil can only be carried out above a temperature of 40°C. In order to determine the solubility of water in oils which remain fluid at 0°C, corn oil at 0.28% FFA and soyabean oil at 0.11% FFA were tested. The results which are shown in Table 1 show that the pattern is the same as for palm oil.

The examination of the various results makes it possible to state tentatively that the solubility of water in vegetable oils is governed by the following equation:

$$S = A + B(\text{FFA}) + C$$

where:

S = the solubility in g% of water;

A = a constant specific to the oil considered;

B = the factor of increase for each percentage unit of FFA;

C = the factor of increase for each degree of temperature;

FFA = free acidity in g% of palmitic acid; and

T = temperature in degree centigrade.

In the case of palm oil of Congo origin, particularly within the range of temperature 50°C to 80°C and the range 0% to 7% FFA, the above equation is expressed by the following:

$$S = 0.198 + 0.0112(\text{FFA}) + 0.00467(t-50)$$

The equation enables an assessment to be made of the solubility in routine conditions

TABLE 1. SOLUBILITY OF WATER AT VARIOUS TEMPERATURE (expressed in % on oil)

Oil	Temperature		
	0°C	40°C	80°C
Corn oil	0.145	0.255	0.375
Soyabean oil	0.090	0.200	0.290

for a naturally acidified oil. In other words, it provides an estimate of the maximum moisture content likely to be found in oil at the outlet of a perfectly set industrial centrifugal purifier in which no dehydration take place as a result of evaporation through contact with air.

It is necessary to point out that the two equations are only rough approximations. They are however sufficiently accurate for routine practice provided they are used within the specified range of temperature and acidity.

In particulars, the effect of temperature must be checked through the use of the general law on solubility equilibrium:

$$\frac{d.\ln S}{dt} = \frac{\Delta H}{RT^2}$$

where:

- S = solubility;
- T = absolute temperature;
- H = heat of solubilization; and
- R = constant of perfect gas.

By integration and conversion to decimal logarithm, the following is obtained:

$$\text{Log. } S = -K \frac{1}{T} + C$$

By plotting log S against the reciprocal of temperature (for two values of T), a straight line is obtained, which makes it possible to read off solubility at any temperature, provided ΔH remains fairly constant over a wide range of temperature.

Vapour Pressure of Water Dissolved in Palm Oil

The need to dehydrate oil to improve its keepability makes it necessary to have a detailed knowledge of the vapour pressure of dissolved water. The knowledge permits to establish the feasibility of industrial drying.

The determination of the water vapour pressure in oil has therefore been undertaken. The apparatus (*Figure 2*) consists of a 250 cc round flask equipped with a mercury manometer and fitted with a lateral tube which is sealed after the flask has been completely evacuated. The flask is then immersed in a thermostatically controlled water bath accurate to the $1/10^{\text{th}}$ of a degree. The changes in mercury level in the monometer are recorded. The moisture content is determined by the acetyl chloride method (33) at the end of a series of recordings at various temperatures. The results are corrected for the following:

- the residual air estimated by a measurement carried out at 0°C on the assumption that at that temperature the atmosphere is saturated with moisture (in our tests, the correction was always lower than 55 mm of mercury); and
- the density of mercury at various temperatures (the correction is very small; of the order of 1 mm of mercury for the higher temperatures).

The results from the determination of moisture content of oil can be accepted without correction for the various temperatures. The accuracy is of the order of 1% when the volumes of the vapour phase and the lipid phase are respectively 50 and 200 cc. The eventual correction is smaller than the titration accuracy.

The results are shown in *Table 2* and are plotted in *Figures 3* and *4* (vapour pressure against moisture content). The solubilities as determined under Solubility of Water in Oil, taking the vapour pressure of free water as corresponding vapour pressure, are also plotted on the graphs.

The results follow fairly closely Henry's law: "The amount of a gas of low solubility, which dissolves in a given mass of liquid at a defined temperature, is directly proportional to the partial pressure of the gas".



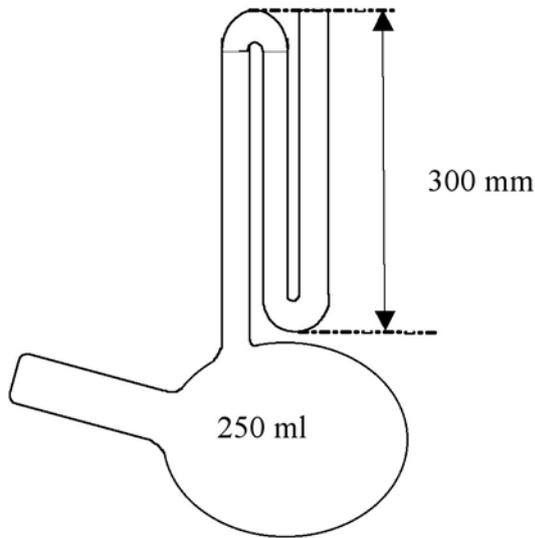


Figure 2. Apparatus for the determination of the vapour pressure of water dissolved in oil.

This makes it possible to establish a priori the equilibrium moisture content, that is the maximum limit of drying that may be attained with air at a given temperature and a known degree of hygrometry. This is because the equilibrium moisture content is equal to the solubility multiplied by the hygrometric degree of the air. A mathematical expression is as follows:

$$H_{eq}^t = S^t K^t$$

where:

H_{eq}^t = equilibrium moisture content at t° ;

S^t = solubility at temperature t° ; and

K^t = hygrometric degree of air at t° .

For technical reasons, no determination of solubility and vapour pressure was carried

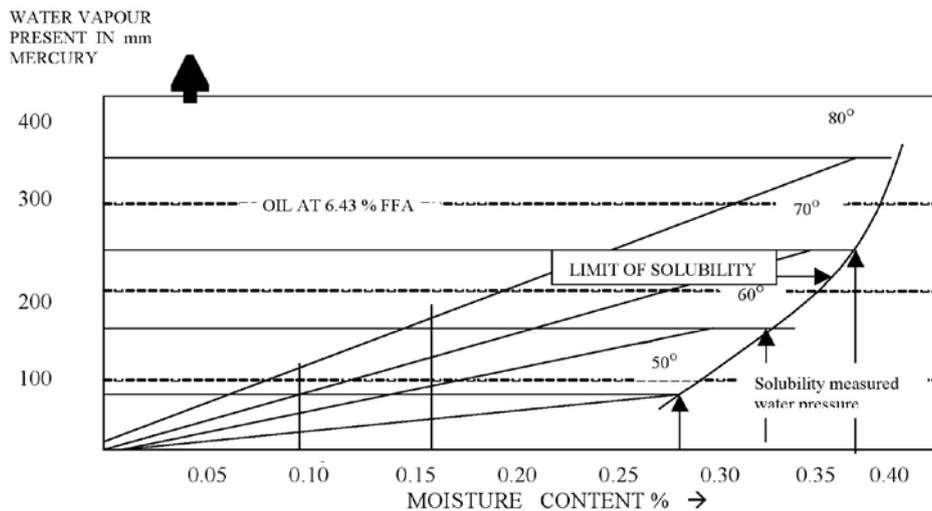


Figure 3. Vapour pressure of water dissolved in oil within the concentration range from nil to solubility limit.

TABLE 2. VAPOUR PRESSURE (mm) OF MERCURY vs. TEMPERATURE

% Moisture	50°C	60°C	80°C	80°C
a) Oil at 6.44% FFA				
Water alone	92 mm	149 mm	234 mm	355 mm
0.16%	52 mm	79 mm	116 mm	157 mm
0.10%	37 mm	51 mm	74 mm	99 mm
0.01%	4 mm	6 mm	8 mm	12 mm
b) Oil at 2.44 % FFA				
0.12%	47 mm	67 mm	88 mm	116 mm

WATER VAPOUR
PRESENT IN mm
MERCURY

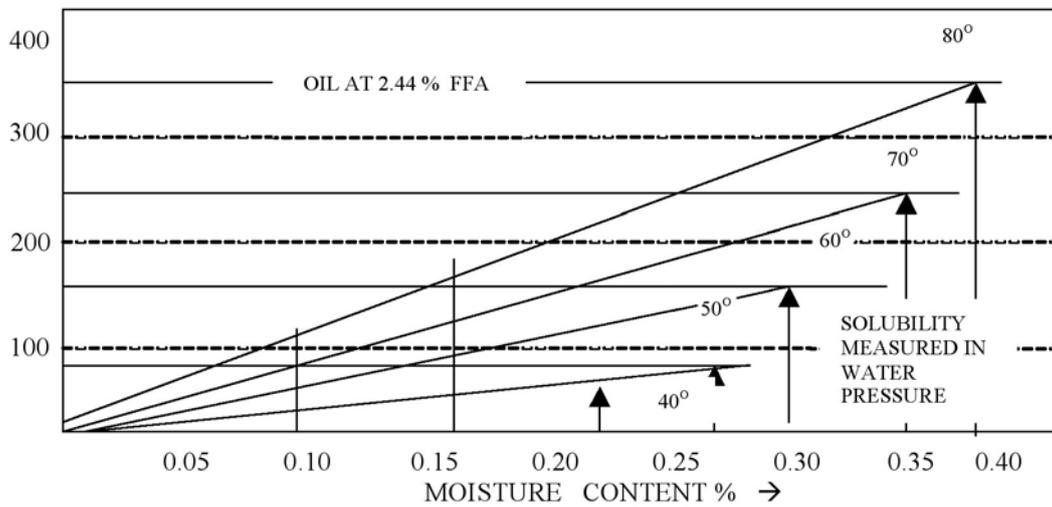


Figure 4. Vapour pressure of water dissolved in oil within the concentration range from nil to solubility limit.

out at 100°C oil within the FFA range 1% to 7% reaches equilibrium for air with water vapour pressure of about 30 mm of mercury (maximum in Congo) when the moisture content of the oil is within the range 0.017% to 0.020%. The latter must be considered as

the limit obtainable for oil at 100°C and air in the Congo. It could be lowered (which does not seem to be of practical value) by increasing the temperature of oil or through desiccation of air.