



Non Dispersive Chemical Deacidification of Crude Palm Oil in Hollow Fiber Membrane Contactor

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Abstract. Performance of chemical deacidification of crude palm oil (CPO) using aqueous NaOH solution in a polysulfone hollow fiber ultrafiltration membrane was investigated. The effects of operating temperature, NaOH concentration and flow rates on percentage of free fatty acids (FFA) removal, oil loss, soap entrainment and overall mass transfer coefficient were evaluated. Overall mass transfer coefficients, soap content in oil and neutral oil loss all increased when the temperature was increased from 60 to 70°C due to an increase of the FFA distribution value. A minimum 0.25 N of NaOH or a NaOH to FFA molar ratio of about 7.62 was required to facilitate the expected extraction efficiency. The increased oil flowrate slightly enhanced the solute transport kinetics, while the aqueous phase flowrate did not significantly influence deacidification efficiency or mass transfer coefficient. About 97% of FFA removal was achieved within 4 hours. The maximum oil loss observed was 11% and the highest soap content in the oil without separation step was 3150 ppm. The values of the overall mass transfer coefficient varied from 2.97×10^{-7} to 7.71×10^{-7} m/s. These results show the potential of using the non dispersive membrane contacting process for chemical deacidification of CPO as well as other vegetable oils.

Keywords: *crude palm oil; free fatty acids; chemical deacidification; alkaline neutralization; hollow fiber membrane contactor.*

1 Introduction

Palm oil is one of the major commercial edible oils from oilseeds and its production expands significantly year by year. In 2014, the annual world production of palm oil was about 62 million metric ton [1]. Due to its massive use for human consumption and growing demand as an alternative energy feedstock, considerable research efforts have been dedicated to finding efficient recovery, refining and utilization methods of palm oil and other vegetable oils.

The non triglyceride materials in crude palm oil (CPO) consist of free fatty acids (FFA), partial acylglycerols, phosphatides, glycolipids, tocopherols, tocotrienols, carotenoids, sterols, methylsterols, triterpene, isoprenoid alcohols, and hydrocarbons [2]. These components are valuable and their recovery from

the oil also increases the quality of the oil in terms of color, taste, odor and stability. In the United States, the term 'refining' refers to FFA reduction or neutralization and its pretreatment step. This so called deacidification process is a critical stage since it affects the oil quality and the overall refining efficiency. The FFA are responsible for undesirable rancid flavor formation (hydrolytic rancidity) and they are more susceptible to oxidation than triglycerides, resulting in a rancid flavor (oxidative rancidity) and reduced nutritional quality [3]. The required quality of neutralized palm oil is a maximum FFA level of 0.25% [4]. The FFA content of the oil should be below 0.5% to give the maximum yield of alkali catalysed transesterification [5].

In the chemical refining process, deacidification is carried out by the addition of alkali (alkaline neutralization) after degumming and prior to bleaching and deodorization. The main drawback of chemical deacidification is excessive loss of triglycerides due to saponification of triglycerides and emulsification of oil to the soaps formed. The neutral oil loss is about 20 to 30% [2]. In the physical refining process, degummed and bleached oil is deacidified during the deodorizing step using steam stripping under high temperature and vacuum condition. Oil loss, amount of water used and effluent to be treated are minimized in this method. However, the high temperature leads to formation of side products such as polymers and trans isomers, and destruction of all carotenes in the oil [3]. Energy consumption is also higher with this method [6].

Various works to overcome the aforementioned disadvantages, including membrane based approaches, have been comprehensively reviewed elsewhere [3,7]. Alkaline neutralization followed by microfiltration seems to be a potential solution for industrial application [8] as it achieved acceptable levels of FFA and phosphorus content. However, the refining efficiency, oil quality and percentage of recovery still need to be optimized. Keurentjes, *et al.* [9] have tried to use a hollow fiber ultrafiltration membrane in membrane based liquid-liquid extraction of FFA from oil using 1,2-butanediol as selective extractant. The loss of triglycerides could be avoided but a high mass transfer resistance resulted, leading to a large membrane area required [3].

Alkaline neutralization is still widely applied in industry since an almost complete deacidification can be gained independent of the initial FFA level. This method can also be adopted easily in small-scale refining practices due to its simplicity and low energy consumption. Because the hollow fiber membrane contactor provides non dispersive contact between two phases, the occlusion of triglycerides into soapstock found in this alkaline neutralization process could be lowered. Further, the reactive nature of sodium hydroxide (NaOH) to FFA results in a higher distribution coefficient of the FFA in this NaOH solution compared with the extractant used in previous membrane extraction work. This

could enhance the mass transfer rate of FFA to the extracting side. The required membrane area can be reduced due to the larger mass transfer. In this research, the performance of a hydrophilic polysulfone hollow fiber ultrafiltration membrane during chemical deacidification of CPO using aqueous NaOH solution was investigated. The effects of operating temperature, NaOH concentration and flow rates on FFA removal percentage, oil loss, soap entrainment and overall mass transfer coefficient were evaluated.

2 Experimental Setup

2.1 Material

The CPO used in this study was kindly supplied by Agrincinal Co., Bengkulu. The CPO was produced in a continuously stirred tank. The initial FFA content of the CPO was 2.8 to 3.5%. Moisture and insoluble impurities content of CPO were 0.3 to 0.57 % and 0.14 to 0.3 % respectively. Density of CPO at 60 °C was 0.882 g/mL. The NaOH (pro analytic) used as reactive extractant was diluted with demineralized water. Chemicals used for sample analysis—*isopropanol* (99 % purity), reagent grade acetone, oxalic acid (pro analytic), analytical grade hydrochloric acid, phenolphthalein indicator solution, bromophenol blue indicator solution and NaOH—were purchased from a local supplier, Bratachem. Demineralized water was available at the laboratory. Refined palm oil was purchased from a local store. Hydrophilic hollow fiber ultrafiltration membranes supplied by GDP Filter, Indonesia were used in the deacidification experiment. The randomly packed polysulfone fibers were potted in epoxy in a polyvinyl chloride (PVC) housing. The hollow fiber module is specified in Table 1.

Table 1 Membrane module specification.

Parameter	Value
Housing material	PVC
Nominal diameter, m	0.051
Fiber material	Polysulfone
Number of fibers	340
Effective length, m	0.3710
Outside fiber diameter, m	0.002
Inside diameter of fiber, m	0.0016
Hydraulic diameter of shell [10], m	0.003825
Fiber thickness, m	0.0002
Inner surface area of lumen, m ²	0.6337
Inner surface area to volume ratio, m ² /m ³	2500
Molecular weight cut-off, Da	20000

2.2 Methods

2.2.1 Distribution Coefficient Measurement

The distribution coefficient was determined as follows. CPO containing FFA was intensively mixed with the desired concentration of aqueous NaOH solution at a 1:1 volume ratio in the temperature controlled stirred tank. The volume of CPO and aqueous NaOH solution was 100 ml each. The temperature was 60°C and the stirring rate was 600 rpm. The combined solution was mixed for 2 hours. The aqueous layer was then separated from the oil. The final concentration of FFA in oil and the final NaOH concentration in aqueous solution were measured to determine the distribution coefficient.

2.2.2 Membrane Deacidification Experiments

Membrane deacidification was carried out in total batch mode using a hollow fiber membrane contactor in which CPO was circulated inside of the fibers cocurrent to aqueous NaOH circulated in the shell side, as shown in Figure 1. Since the membrane was a hydrophilic polysulfone membrane, the aqueous NaOH phase would wet the membrane and then the pores were expected to be filled with aqueous NaOH phase with no further dispersion into the oil phase.

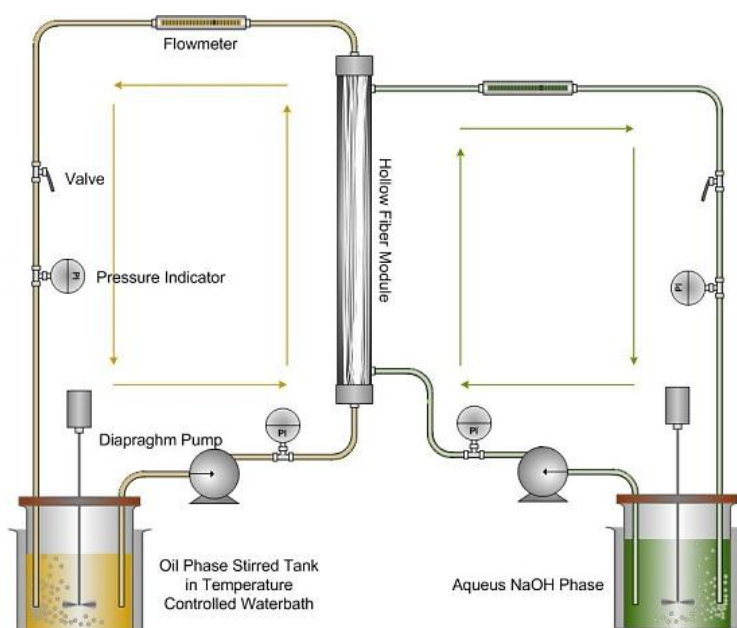


Figure 1 Experimental setup.

Freshly prepared CPO with a given initial percentage of FFA and NaOH at variable concentrations in the tank was then circulated with controlled pressure and flowrate of each phase. In the outlet of the module, about 0.3 bar higher pressure was applied on the oil phase (lumen side) to prevent phase dispersion. The temperatures of both oil and aqueous phase tank were controlled using a water bath. The initial volume of NaOH in the tank was 3000 ml, 3 times larger than the oil in the aqueous phase tank to keep the diluted soap concentration in the aqueous phase. Samples from the oil and aqueous phase tanks were taken periodically. Both the percentage of FFA in the oil phase samples and the NaOH concentration in the aqueous phase samples were measured to determine the percentage of FFA removal and overall mass transfer coefficient. The soap content in the oil phase samples and the final oil solution volume in the oil phase tank were also measured. Both the lumen and shell side of the module were washed with demineralized water, followed by refined palm oil rinsing for the lumen side and aqueous NaOH (with a concentration similar to the primary experiment's concentration) flushing for the shell side prior to each deacidification experiment. When the experiment was completed, the membrane module was cleaned (recirculated) with demineralized water at 60°C for a couple of times, followed by washing with demineralized water.

2.3 Data Analysis

2.3.1 Sample Analysis

The FFA content (%-wt) in the CPO and the soap content (ppm) in the oil were analysed by NaOH titration (AOCS Ca 5a-40) and acid titrimetric method (AOCS Cc 17-79) [11], respectively. NaOH concentrations were measured by titration with oxalic acid. For calculation of the distribution coefficient, the difference between the initial and final FFA in oil was considered as the final FFA in aqueous NaOH. In the determination of the distribution coefficient and experimental overall mass transfer coefficient, the FFA percentage was converted to molar concentration units. In this experiment, we assume the FFA to be palmitic acids.

2.3.2 Percentage of FFA Removal

In a batch recirculation operation, the percentage of FFA removal (*PE*) is described by comparing the concentration of solute in the reservoir at any time to the initial concentration of solute in the reservoir, as follows:

$$PE(\%) = 1 - \frac{\% FFA|_{t=t}}{\% FFA|_{t=0}} \times 100 \quad (1)$$

2.3.3 Oil Loss

In this experiment, a difference was found between the actual oil mass with the oil mass that should have remained in the reservoir after 4 hours of membrane deacidification. This is subjected to neutral oil loss governed by the following equation:

$$P_{OL} = \frac{M_{fs}|_{t=end} - M_{fa}|_{t=end}}{M_{fs}|_{t=end}} \times 100\% \quad (2)$$

where P_{OL} is percentage of oil loss, M_{fa} is actual oil mass, and M_{fs} is final oil mass without loss. Both mass values were determined at the end of deacidification. M_{fa} and M_{fs} are defined as follows:

$$M_{fs}|_{t=end} = \text{initial mass of oil} - \text{total mass of oil taken as samples} - \text{total mass FFA neutralized} \quad (3)$$

$$M_{fa}|_{t=end} = \text{Mass of oil remained in tank} - \text{mass of soaps in oil} \quad (4)$$

2.3.4 Experimental Mass Transfer Coefficient

In the liquid-liquid membrane extraction process, the solute concentration gradient between the phases drives the solutes transport. The mass transfer rate of solutes from the feed phase (N_A) can be expressed as [12]:

$$N_A = k_f A_f (C_{Af} - C_{Afi}) \quad (5)$$

where k_f is the mass transfer coefficient, A_f the surface area on the feed side, C_{Af} and C_{Afi} are the concentrations at bulk feed phase and feed side of feed-extractant interphase respectively. C_{Afi} is always in equilibrium with the concentration of solute in the extractant side of feed-extractant interphase C_{Afw} , as stated in the following equation:

$$D_E = \frac{C_{Afw}}{C_{Afi}} \quad (6)$$

where D_E is the distribution coefficient of solutes between the two phases. In this study, D_E represents the distribution of FFA between aqueous NaOH and oil phase and can later be written as a function of sodium hydroxide.

In the hollow fiber module, the transport of solute takes three steps from feed to extractant phase through the organic feed phase boundary layer, inside the membrane pores and through the aqueous extractant phase boundary layer. The

overall mass transfer coefficient can be estimated using resistance in a series model related to three local resistances [13-15]. The NaOH used here was very reactive to FFA. Therefore the FFA was neutralized as it reached the interphase. In other words, this gave a high distribution of FFA in the aqueous phase, which will be obvious in the later discussion of the distribution coefficient as a function of the NaOH concentration. Employing a hydrophilic membrane where pores are filled with solute (in this case FFA), the preferred phase can reduce additional resistance in the membrane pores [16-18].

In terms of overall transport resistance, the mass transfer rate of solutes (N_A) from feed phase to extractant phase is then governed by the following equation:

$$N_A = K_a A_f \left(C_{Af} - \frac{C_{Aw}}{D_E} \right) \quad (7)$$

where C_{Aw} is the concentration of solute in the bulk aqueous phase. In this experiment, the overall mass transfer coefficient K_a was obtained from the experimental data by solving the mass balance of solute in both membrane and reservoir.

The oil feed phase and aqueous reactant phase were recirculated in cocurrent flow. The two main governing equations describing solute depletion in the feed phase are [10,19]:

Mass balance in the module:

$$\frac{\partial C_{Af}(x,t)}{\partial A_x} = -\frac{K_a}{Q_f} \left(C_{Af}(x,t) - \frac{C_{Aw}(x,t)}{D_E(t)} \right) \quad (8)$$

Mass balance in the reservoir:

$$\frac{\partial C_{Af}^{in}(t)}{\partial t} = -\frac{Q_f}{V_f} (C_{Af}^{in}(t) - C_{Af}^{out}(t)) \quad (9)$$

where Q_f is the flow rate of the oil feed phase, V_f is the volume of the oil in the feed reservoir, A_x the membrane area at position x of the module's length, $C_{Af}(x,t)$ is the solute concentration at position x of the module's length. $C_{Af}^{in}(t)$ and $C_{Af}^{out}(t)$ are the solute concentrations in the feed inlet and outlet of the module at any time, respectively.

The two ordinary differential equations above can be solved using initial conditions $C_{Af}^{in}(t) = C_{Af;io}^{in}(t)$ and $C_{Af}(0,t) = C_{Af}^{in}(t)$. Further, the concentration of

solute in the reactant phase $C_{Aw}(x,t)$ in Eq. (8) can be obtained by solving the overall mass balance in the module:

$$Q_f \left(C_{Af}^{in}(t) - C_{Af}(x,t) \right) = Q_w \left(C_{Aw}(x,t) - C_{Aw}^{in}(t) \right) \quad (10)$$

where $C_{Aw}^{in}(t)$ is provided by the overall mass balance in the reservoir

$$V_f \left(C_{Af}^{in}(0) - C_{Af}^{in}(t) \right) = V_w C_{Aw}^{in}(t) + 0 \quad (11)$$

The value of $D_E(t)$ in Eq. (8) varies with time since it is a function of the sodium hydroxide concentration, which will be explained in the next section. The sodium hydroxide concentration itself was assumed constant along the membrane module and similar to the concentration in the tank at any arbitrary point of time. The value of K_a was determined by numerically solving Eqs. (8-11) in Microsoft Excel™.

The mass balance in the reservoir was first solved using Euler's method to obtain $C_{Af}^{out}(t)$. At any point, Eq. (9) becomes:

$$C_{Af}^{out}(j) = \frac{V_f}{\Delta t \cdot Q_f} \left(C_{Af}^{in}(j+1) - C_{Af}^{in}(j) \right) + C_{Af}^{in}(j) \quad (12a)$$

and at the end:

$$C_{Af}^{out}(j) = \frac{V_f}{\Delta t \cdot Q_f} \left(C_{Af}^{in}(j) - C_{Af}^{in}(j-1) \right) + C_{Af}^{in}(j) \quad (12b)$$

The mass balance in the module was then solved using the 4th order Runge Kutta method to provide $C_{Af}(L_m,t)$, the solute concentration at position L_m of the module. Eqs. (8) and (10-11) become:

$$C_{Af}(i+1, j) = C_{Af}(i, j) + \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4) \quad (13)$$

where

$$k_1 = -\frac{K_a}{Q_f} \left(C_{Af}(i, j) - \frac{C_{Aw}(i, j)}{D_E(j)} \right) \cdot \Delta A_m \quad (14a)$$

$$C_{Aw}(i, j) = \frac{Q_f}{Q_w} \left(C_{Af}^{in}(j) - C_{Af}(i, j) \right) + \frac{V_f}{V_w} \left(C_{Af}^{in}(0) - C_{Af}^{in}(j) \right) \quad (14b)$$

$$k_2 = -\frac{K_a}{Q_f} \left(\left(C_{Af}(i, j) + \frac{k_1}{2} \right) - \frac{C_{Aw}(i, j)}{D_E(j)} \right) \cdot \Delta A_m \quad (14c)$$

$$C_{Aw}(i, j) = \frac{Q_f}{Q_w} \left(C_{Af}^{in}(j) - \left(C_{Af}(i, j) + \frac{k_1}{2} \right) \right) + \frac{V_f}{V_w} \left(C_{Af}^{in}(0) - C_{Af}^{in}(j) \right) \quad (14d)$$

$$k_3 = -\frac{K_a}{Q_f} \left(\left(C_{Af}(i, j) + \frac{k_2}{2} \right) - \frac{C_{Aw}(i, j)}{DE(j)} \right) \cdot \Delta A_m \quad (14e)$$

$$C_{Aw}(i, j) = \frac{Q_f}{Q_w} \left(C_{Af}^{in}(j) - \left(C_{Af}(i, j) + \frac{k_2}{2} \right) \right) + \frac{V_f}{V_w} \left(C_{Af}^{in}(0) - C_{Af}^{in}(j) \right) \quad (14f)$$

$$k_4 = -\frac{K_a}{Q_f} \left(\left(C_{Af}(i, j) + k_3 \right) - \frac{C_{Aw}(i, j)}{DE(j)} \right) \cdot \Delta A_m \quad (14g)$$

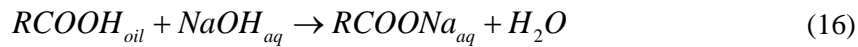
$$C_{Aw}(i, j) = \frac{Q_f}{Q_w} \left(C_{Af}^{in}(j) - \left(C_{Af}(i, j) + k_3 \right) \right) + \frac{V_f}{V_w} \left(C_{Af}^{in}(0) - C_{Af}^{in}(j) \right) \quad (14h)$$

Eqs. (13) and (14a-h) were solved by iteratively guessing the value of K_a until $C_{Af}(A_m, j)$ meets the value of $C_{Af}^{out}(j)$ from Eqs. (12a) and (12b). A_m is the membrane specific area at membrane module length equal to L_m . The coefficient of determination (R^2) was used as basis of the optimization [19], as follows:

$$R^2 = 1 - \frac{\sum_{j=0}^{j=j} \left(C_{Af}(A_m, j) - C_{Af}^{out}(j) \right)^2}{\sum_{j=0}^{j=j} \left(C_{Af}(A_m, j) - \bar{C}_{Af}^{out}(j) \right)^2} \quad (15)$$

2.3.5 Distribution Coefficients

Experimental overall mass transfer coefficient calculations require the value of the distribution coefficient. The alkaline neutralization reaction of FFA with NaOH can be described with the following equation:



In this reaction the equilibrium favors the aqueous phase since the FFA react instantaneously with sodium hydroxide. The equilibrium constant, K_{eq} is expressed as follows:

$$K_{eq} = \frac{[RCOONa_{aq}]}{[RCOOH_{oil}][NaOH_{aq}]} \quad (17)$$

The distribution coefficient of FFA between aqueous and oil phase in Eq. (6) can be related to the equilibrium constant and written as a function of sodium hydroxide:

$$K_{eq} = \frac{D_E}{[NaOH_{aq}]} \quad (18)$$

$$D_E = K_{eq} [NaOH_{aq}] \quad (19)$$

When Eq. (19) is linearized, K_{eq} can be obtained by making a log-log plot of distribution coefficient versus equilibrium concentration of NaOH. A linear curve with its slope equal to 1 provides the value of $\log K_{eq}$ as intercept.

In the alkaline neutralization of oil, saponification of neutral oil also occurs. Since the neutralization reaction is the only process considered in this work, the parameters are called as apparent distribution coefficient. In order to obtain a valid model, the equilibrium experiments were conducted with the amount of NaOH below the stoichiometric value to neutralize the FFA.

3 Results and Discussion

3.1 Effect of Temperature

The distribution coefficient of FFA and the equilibrium concentration of NaOH were investigated at temperatures of 60 and 70°C. The equilibrium coefficients (K_{eq}) resulted from linear regression are presented in Figure 2. The equilibrium coefficient at 60°C was $1 \times 10^{2.0538}$ L/mol, while K_{eq} was $1 \times 10^{2.0978}$ L/mol at 70°C. The higher equilibrium coefficient at higher temperature is mainly caused by the viscosity properties of the oil and emulsification phenomena. The viscosity of the vegetable oil decreases exponentially with an increase of the temperature [20]. The viscosities (cp) of palm oil are 96.3, 40.4, 33.3, and 27 for temperatures (°C) of 35, 40, 45, and 50, respectively [21].

The FFA available to react with the NaOH in the solution was lower at reduced temperature. According to the Wilke Chang equation [22], the solute diffusivity is directly affected by the solvent viscosity coupled with the temperature itself. Also at low temperature, the resulted soaps and oil tend to form emulsion. The less oil in free form, the smaller the FFA concentration in the reaction interface to interact with the NaOH.

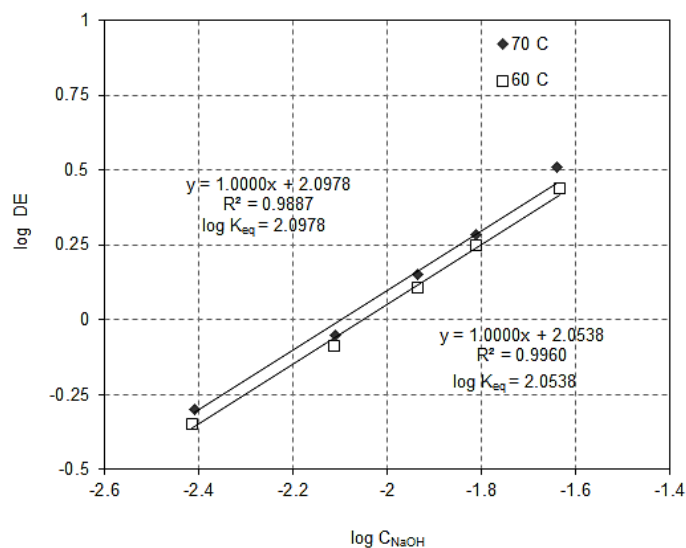


Figure 2 Distribution coefficient (log) of FFA versus equilibrium concentration (log) of NaOH at various temperature; Initial FFA percentage: 2.69-2.80 %; Initial NaOH to FFA molar ratio: 0.365-0.977; NaOH to oil volume ratio: 1.

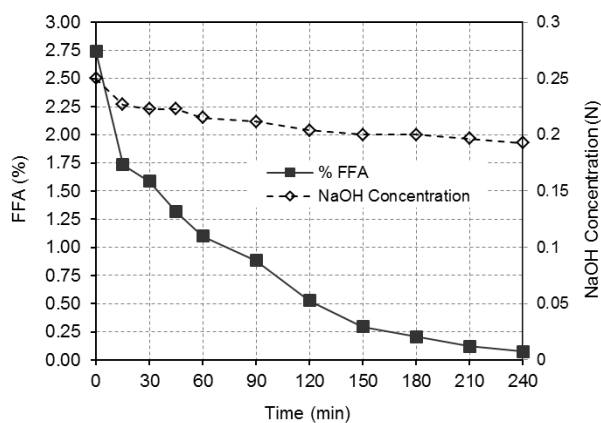


Figure 3 Percentage of FFA and NaOH concentration versus time at 60°C; initial NaOH (0.25 N) to FFA molar ratio: 7.6; NaOH to oil (1000 ml) volume ratio: 3; equal oil and NaOH phase flow rates (800 ml/min).

Total batch recirculation was conducted to investigate the influence of temperature on membrane deacidification. The typical results of FFA content (%-wt) and NaOH concentration in the tanks during 4 hours of extraction are shown in the Figure 3. The membrane deacidification process parameters were

subsequently calculated using the methods presented in the previous section. The percentage of FFA removal and the overall mass transfer coefficient of the above temperatures at an initial NaOH concentration of 0.25 N or an initial NaOH to FFA molar ratio of 7.6 and equal phase flowrates are presented in Figure 4. A high percentage of FFA removal was achieved at an early time in our deacidification configuration and after 4 hours of batch membrane deacidification about 98% of FFA was removed at 70°C and about 97% was removed at 60°C. These results agree well with the equilibrium data and may suggest that the higher distribution of FFA at higher temperature enhances the rate of FFA transport. A more obvious increase was observed in terms of the overall mass transfer coefficient. Other coupling influences of temperature on physicochemical properties, such as density, viscosity and diffusivity affect the transport rates in the same direction.

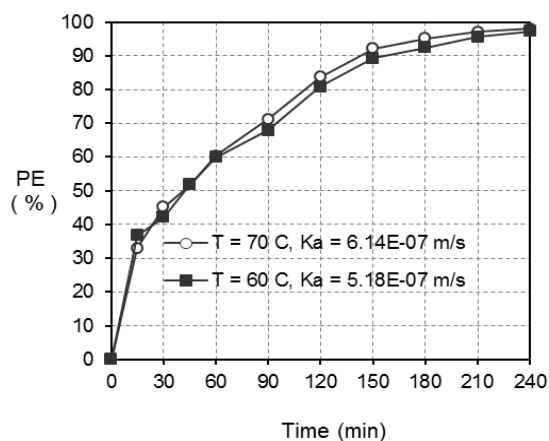


Figure 4 Percentage of FFA extraction (PE) versus time at various temperatures; initial NaOH (0.25 N) to FFA molar ratio: 7.6; NaOH to oil (1000 ml) volume ratio: 3; equal oil and NaOH phase flow rates (800 ml/min).

Zuo, *et al.* [23] have examined the expected but rarely reported advantage of non dispersive membrane extraction. Compared with 200 ppm of solvent entrainment found in the classical liquid-liquid extraction, the membrane based approach in their work could reduce the solvent entrainment to 10 ppm. However, negligible entrainment is hard to achieve due to the occurrence of emulsification phenomena of oil and soaps. Both oil phase and soap containing aqueous NaOH phase tend to attract each other, causing phase dispersion. The results in Table 2 show that both oil loss and soap entrainment in oil phase increased with an increase of temperature. As mentioned before, the degree of removal was higher at 70°C, resulting in a larger amount of soaps formed. Emulsification of oil and soaps was then enhanced. The saponification of

triglycerides remained low when the temperature was increased from 60 to 70°C relative to the neutralization reaction indicated by the slight increase of oil loss, from 6.6 to 8.1%. These results show the potential of the membrane contactor for selective neutralization of FFA in oil. Compared with the oil loss, a significant rise was found in soap entrainment (about 50%). At high temperature the solubility of soap in oil is greater. Meanwhile, at lower temperature oil tends to be in aggregates [8]. This will lead to easy occlusion of soaps formed with oil when the temperature is raised. It possibly implies that deacidification at 60°C should be preferred over 70°C since the percentage of FFA removal is not much lower while it has the benefit of reduced phase dispersion.

Table 2 Neutral oil loss and soap entrainment after 4 hours of extraction at various temperatures; initial NaOH (0.25N) to FFA molar ratio: 7.6; NaOH to oil (1000ml) volume ratio: 3; equal oil and NaOH phase flowrate (800 ml/min).

Temperature (°C)	Oil loss (%)	Soap in oil (ppm)
60	6.6	2110
70	8.1	3150

3.2 Effect of Sodium Hydroxide Concentration

The effect of reactant concentration was examined by conducting the experiment with NaOH concentrations ranging from 0.1 to 0.5 N at 60°C at equal phase flowrate. As shown in Figure 5, low FFA removal efficiencies and overall mass transfer coefficients were obtained at NaOH concentrations below 0.25 N or an NaOH to FFA molar ratio of 7.6. About 87% of FFA recovery was reached within 4 hours of operation at an NaOH concentration of 0.2 N. It is clearly indicated in Eq. (19) that the distribution coefficient is a function of the NaOH concentration. Therefore, at low NaOH concentrations both the concentration gradient and the overall mass transfer coefficient will be smaller as they depend on the distribution value. Although the NaOH to FFA molar ratio is stoichiometrically more than sufficient, the slow diffusion of NaOH limits the available concentration at interphase. Gonzalez-Munoz, *et al.* [10] reported the typical result that it is necessary to utilize a ratio of at least 4 to remove 97% phenol from organic solution with aqueous NaOH. In the present work, more than 97% recovery of FFA was successfully obtained at an NaOH to FFA molar ratio of 7.62.

The lower FFA removal rate at NaOH concentrations below 0.25 N also provides a good explanation for the soap entrainment in Figure 6. The soap content increased with the NaOH concentration, which slightly differed when the NaOH concentration was varied from 0.25 to 0.5 N. The amount of soaps formed by the neutralization reaction determines how much soap and its aqueous phase can dissolve to the oil phase. It is shown that once-through

operation and simultaneous recovery of soaps from the aqueous phase would be necessary in lowering the soap entrainment itself and the emulsification phenomena, further increasing the availability of NaOH in the reaction front.

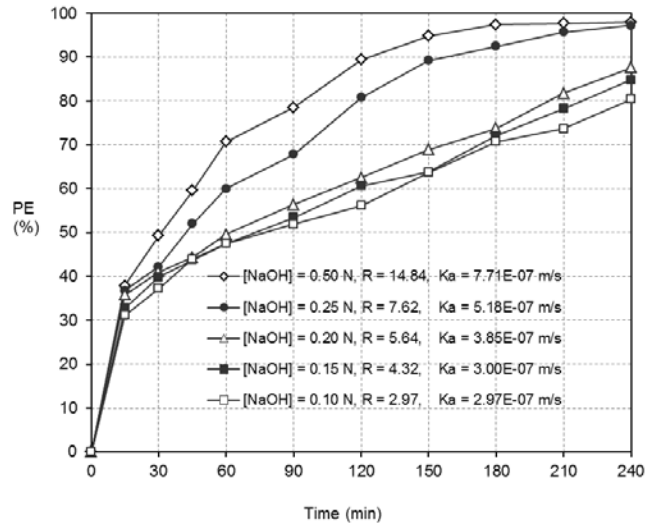


Figure 5 Percentage of FFA extraction versus time at various NaOH concentrations; NaOH to oil (1000 ml) volume ratio: 3; equal oil and NaOH phase flowrates (800 ml/min); 60°C.

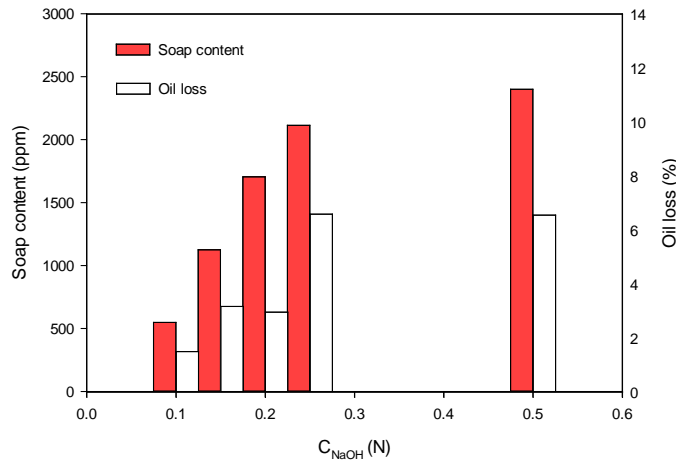


Figure 6 Neutral oil loss and soap entrainment after 4 hours of extraction at various NaOH concentrations; NaOH to oil (1000 ml) volume ratio: 3; equal oil and NaOH phase flowrates (800 ml/min); 60°C.

A similar result for oil loss at various NaOH concentrations is depicted in Figure 6. The overall mass transfer coefficient values in the concentration range of 0.1 and 0.2 N were quite similar, although the NaOH to FFA molar ratios increased. Since the saponification is subjected to neutral oil loss, this side reaction could have greater influence in this NaOH concentration range. Above this NaOH concentration value the selectivity of deacidification was maintained as indicated by the increasing overall mass transfer coefficient and unchanging oil loss between 0.25 and 0.5 N. In addition to selectivity, the slightly rising value of soaps in oil at this range can also be useful as justification for the non dispersive nature of this membrane process.

3.3 Effect of Flowrates

Figures 7 and 8 show the effects of flowrates of oil and aqueous phases on the percentage of FFA removal, respectively. It can be seen in Figure 7 that the increase of the oil flowrate from 600 to 1000 ml/min, while maintaining a constant aqueous rate, slightly enhanced the solute transport kinetics. The mass transfer coefficient was found to be in the range of 4.81×10^{-7} to 7.03×10^{-7} m/s. On the other hand, when the aqueous NaOH flow rate was varied from 400 to 800 ml/min and the oil flow rate was kept at 800 ml/min, its effect on the percentage of FFA removal and the overall mass transfer coefficient was practically not apparent. These results show that the variation in the flowrate of the aqueous sides is less significant in this membrane deacidification process. This result also suggests that at NaOH to FFA molar ratios higher than 6.8 the contribution of the concentration gradient to the transport rate is favorable rather than the kinetics.

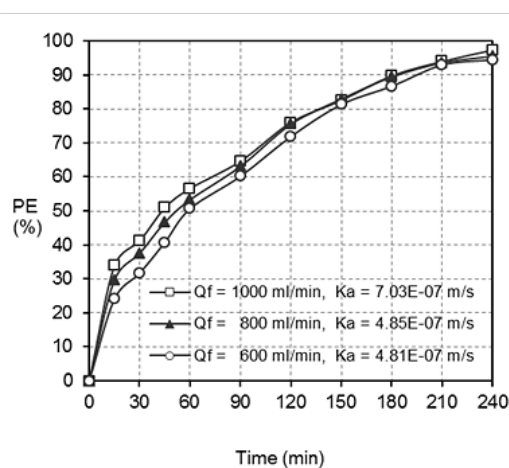


Figure 7 Percentage of FFA extraction versus time at various oil flow rates; NaOH to oil (1000 ml) volume ratio: 3; initial NaOH (0.25 N) to FFA molar ratio: 6.8; NaOH phase flowrate 800 ml/min; 60°C.

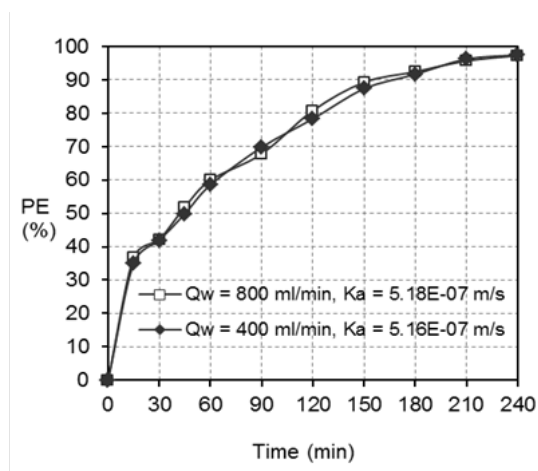


Figure 8 Percentage of FFA extraction versus time at various NaOH flowrates; NaOH to oil (1000ml) volume ratio: 3; initial NaOH (0.25N) to FFA molar ratio: 7.6; oil phase flowrate 800 ml/min; 60°C.

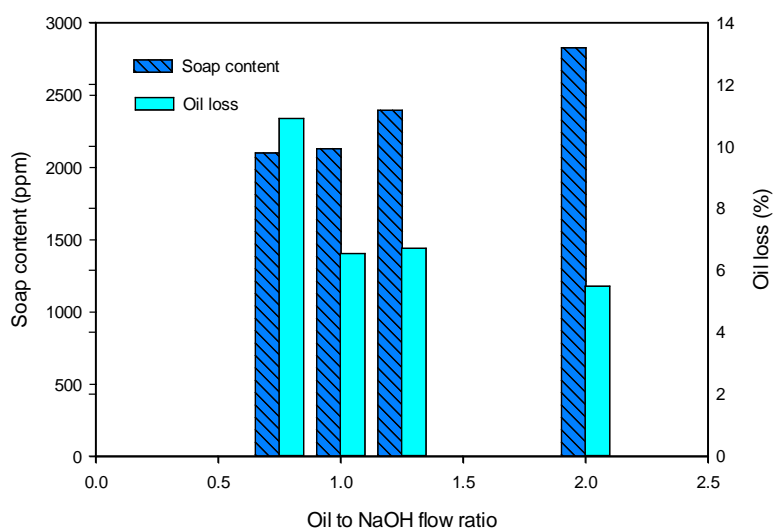


Figure 9 Neutral oil loss and soaps entrainment after 4 hours of extraction at various oil to NaOH volumetric flow ratios; NaOH to oil (1000ml) volume ratio: 3; initial NaOH (0.25N) to FFA molar ratio: 6.8; 60°C.

Comparing each phase volumetric flow rate to its opposite, the more obvious entrainment finding is presented in the Figure 9. When the oil flowrate is greater than the aqueous flow rate, the soap content in the oil increased and in contrast the oil loss increased. As the flow rate of one phase was higher, it attracted the

opposite phase. In the conventional dispersive gas-liquid contacting, at high gas velocity the gas may carry over liquid as a mist [24]. It is mentioned that in this membrane deacidification study, the emulsification phenomena enhanced occlusion of both phases. This generates a slight but tolerable phase entrainment that is not found in other membrane extraction processes. A significant oil loss was found when the oil phase volumetric flowrate was lower than the aqueous phase volumetric flowrate. This could also be attributed to unfavorable selectivity of the neutralization rate due to slow solute diffusion on the oil layer at lower oil flowrates. Deacidification at oil to NaOH volumetric flow ratios of 1 to 1.25 is recommended, which contributes to modest results in terms of oil loss and soap content.

3.4 Process Potentials

The results of alkaline neutralization in this non dispersive mode provide a promising alternative to the conventional one, especially in terms of neutral oil loss and soap content in oil. In conventional alkaline neutralization [2,4], the soapstock and neutralized oil mixture are separated in a centrifugal separator. The discharged oil contains 500-1000 ppm of soap. About 10-20% hot water is then added to the oil before undergoing a second centrifugal separation step. The final soap concentration is less than 50 ppm. Although it gives the expected FFA level, the main neutralization step with its successive post treatment yields a total oil loss of about 20-30 %. In our proposed non dispersive neutralization system, the observed maximum oil loss was 11% and the highest soap content in oil without separation step was 3152 ppm. These findings promise a significant potential reduction of oil loss and elimination of the first centrifugal separation step. To be considered is the fact that centrifugal separation has a very low capacity of each unit. Another potential is shown by the lower operating temperature of this mode, even for highly viscous palm oil. In the conventional process, the suggested temperature of operation to avoid emulsion formation is 90-95°C. Due to the non dispersive nature and lower operating temperature of the proposed oil neutralization system, its effect on oil composition and heat stability would be somewhat better than with the conventional method.

Membrane based solvent extraction of fatty acids with butanediol as selective extractant in Keurentjes, *et al.* [9] was considered to be unattractive due its high resistance. The authors reported that the overall mass transfer coefficient increased with a decrease in fatty acid chain length. The overall mass transfer coefficient value was in 10^{-8} m/s order of magnitude for C14 to C18. The cellulose membrane used had a cutoff of about 6000 Da with a fiber thickness of 8 μm . The major fatty acids of palm oil are C16 and C18. In our experiment on membrane based alkaline neutralization of palm oil we used 20000 Da

polysulfone membranes with a wall thickness of 200 μm. The overall mass transfer coefficients varied from 2.97×10^{-7} m/s to 7.71×10^{-7} m/s for complete FFA recovery. Although we used a membrane with significantly larger thickness, the resulting mass transfer coefficients were one order of magnitude higher than in the previous work. It is obvious from the literature [13-15] that membrane resistance is proportional to membrane thickness. It becomes clear that the use of NaOH as reactive extractant greatly enhances the mass transfer coefficient. The required membrane area can then be lowered. For a once-through operation, the membrane area can be calculated by solving Eqs. (8) and (10), resulting in a common equation for conventional contacting equipment, $NTU=L/HTU$ [9], as follows:

$$\ln \left[\frac{\left(C_{Af}(x) \left(1 + \frac{Q_f}{D_E Q_w} \right) - \left(\frac{Q_f}{D_E Q_w} C_{Af}^{in} \right) \right)}{\left(1 + \frac{Q_f}{D_E Q_w} \right)} \right]_{C_{Af}^{in}}^{C_{Af}^{in}(L_m)} = \frac{K_a}{Q_f} A_m \quad (20)$$

In this experiment, it would require 105.78 m² of membrane area (167 modules) to reduce the FFA level in palm oil from 5% to 0.25% with once-through operation, at a constant concentration of NaOH (0.25N), temperature of 60 °C, oil flow rate 800 ml/min (linear velocity, $v = 0.0195$ m/s or equal to Reynold number, $Re = 1.44$), and aqueous NaOH flowrate 800 ml/min ($v = 0.0137$ m/s or $Re = 91.62$). For 5 m³/hr of oil, the deacidification of this scheme requires a membrane area of 11018.34 m² (105 × 167 modules).

Further interesting work, along with true optimization of this membrane deacidification process, concerns incorporation with the degumming step and exploitation of the membrane process for separating soaps from neutralized oil. A successful integration would enable application of the proposed deacidification method in vegetable oil refining or as the pretreatment step of biodiesel feedstock.

4 Conclusion

The hydrophilic hollow fiber ultrafiltration membrane contactor provides good performance in the caustic deacidification of CPO, reducing FFA content in oil to an acceptable level. Mass transfer coefficients were one order of magnitude higher than in the previous membrane extraction work. Overall mass transfer coefficients, soap contents in oil and neutral oil loss all increased when the temperature was increased from 60 to 70°C due to an increase of the FFA distribution value. A minimum 0.25 N of NaOH or a NaOH to FFA molar ratio

of about 7.62 was required to facilitate the expected extraction efficiency. The increased oil flowrate slightly enhanced the solute transport kinetics, while the aqueous phase flowrate did not significantly influence the membrane deacidification efficiency or mass transfer coefficient. About 97% of FFA removal was achieved within 4 hours. The maximum oil loss observed was 11% and the highest soap content in oil without separation step was 3150 ppm. The values of the overall mass transfer coefficient varied from 2.97×10^{-7} to 7.71×10^{-7} m/s. These results show the potential of using the non dispersive membrane contacting process for chemical deacidification of CPO and as well as other vegetable oils.

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Nomenclature

Symbols

A_m	membrane surface area (m^2)	N_A	fatty acid rate (mol/s)
C_A	concentration of fatty acids (mol/m^3)	Q	volumetric flowrate (m^3/s)
D_E	distribution coefficient	R^2	coefficient of determination
k	local mass transfer coefficient of fatty acids (m/s)	Re	Reynolds number
K_a	overall mass transfer coefficient (m/s)	t	time (s)
K_{eq}	equilibrium coefficient	v	linier velocity (m/s)
L_m	membrane length (m)	V	volume (m^3)
M	mass (g)	x	distance along the fiber (m)

Subscripts

A	fatty acid	f_w	aqueous side in the oil-aqueous interface
end	final condition	m	membrane
f	feed solution	w	aqueous solution
f_i	feed side in the oil-aqueous interface	0	initial condition

Superscripts

in	module inlet
out	module outlet
-	average

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