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SIMULTANEOUS DEGUMMING AND DEACIDIFICATION OF CRUDE PALM OIL USING POLYMERIC HOLLOW FIBER MEMBRANES

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ABSTRACT

The performances of two self-made polyvinylidene fluoride (PVDF) membranes made of different polymer concentration were studied in removing free fatty acid (FFA) and phospholipids from crude palm oil (CPO). Results showed that 18PVDF membrane (18wt% polymer) exhibited lower oil flux (2.07 kg/m^2.h) compared with the 14PVDF membrane (2.4 kg/m^2.h), owing to its relatively smaller pore size. The smaller pore size of 18PVDF membrane have resulted in higher phosphorus rejection i.e. 93% compared with 80% rejection reported in 14PVDF membrane in the refining process without addition of chemicals. It is also found that the use of phosphoric acid in the conventional chemical refining process was ineffective in improving membranes' phosphorus rejection. Both membranes showed significant decline in phosphorus removal, owing to the drastic increase in phosphorus content of feed CPO upon addition of phosphoric acid. With respect to FFA reduction, it is found that no membrane could eliminate FFA in the CPO in the absence of NaOH. Despite there was a need to use NaOH, the elimination of phosphoric acid usage coupled with no wastewater produced (from the oil washing process) have made membrane technology to be more techno-economically and environmentally friendly than the conventional technology.

Keywords*: membrane, crude palm oil, deacidification, degumming, free fatty acid*

INTRODUCTION

Palm oil which derived from the fruits of palm trees is the common cooking ingredient in the tropical belt of Southeast Asia, Africa and parts of Brazil. Besides being cooking oil, palm oil can also made into margarine, specialty fats and oleochemicals. Its increasing use in commercial food industry is mainly due to its many nutritional advantages such as free of cholesterol, rich in natural anti-oxidant and high content of natural carotenoids [1].

In palm oil industry, refining process in general involves removal of undesirable constituents such as free fatty acid (FFA), phospholipid (PL), colour pigment and trace metals from crude palm oil (CPO), making the refined oil meeting acceptable effects on color, taste, odor and stability. Industrially the two most commonly used methods for CPO refining are chemical and physical steam refining. Despite being able to remove or partially remove the impurities at different stages of refining, these two conventional refining methods are associated with several significant drawbacks such as loss of neutral oil and nutrients, high energy consumption, huge usage of water and chemicals, leading to a loss in overall profit. Furthermore, water which is used for oil washing during chemical refining process could generate heavily polluted effluent which in turn requires additional wastewater treatment process. For more details on the pros and cons of the conventional refining processes, one can refer to a review article authored by Bhosle and Subramanian in 2005 [2].

Over the years, many alternative refining processes namely biological deacidification by using specific microorganisms, chemical reesterification, supercritical fluid extraction and membrane technology have been introduced in an effort to replace the conventional refining processes. Of these new approaches proposed, membrane technology seems to be the most potential alternative solution to edible oil production. The successful implementation of membranes in different kinds of industries such as water and wastewater treatment [3], seawater/brackish water desalination [4], drug delivery [5], food and beverage processing [6], etc have convinced the researchers the possibility of extending membrane technology to other industrial areas.

In the past decade, many reports on vegetable oil refining using membrane-based technology have been documented and conceptually, membranes can be used in almost all stages of oil production and purification [7-15]. Table 1 summarizes the use of different membrane categories in the refining process of vegetable oils. As can be seen from the table, several drawbacks of using membrane e.g. use of hexane and alcohol, requires relatively high operating pressure and fouling problem are the major obstacles preventing rapid adoption of membrane technology in industrial applications. Despite showing huge potential in removing PLs from the oils, the elimination of FFA using membrane however was reported to be ineffective and strongly depended on the chemicals used. To our best knowledge, there is a little work on membrane vegetable oil refining without the use of solvent in FFA reduction. Due to this point, we have made an attempt to refine CPO using microporous hollow fiber membranes to overcome the drawback of current refining process.

The objective of this study is to investigate the efficiency of in-house made polyvinylidene fluoride (PVDF) hollow fiber membranes in removing impurities i.e. PL and FFA from CPO. The performance of membrane will be first examined in the CPO refining process in the absence of NaOH and H_3PO_4. It will be followed by another performance evaluation with the addition of H_3PO_4. Lastly, the effect of NaOH quantity on the oil quality will be conducted to identify the optimized amount of alkali needed to achieve complete FFA elimination. The results obtained will then be analyzed and discussed in order to provide in-depth understanding on the potential of using membranes in CPO refining process.

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Table 1: Summary of some membrane technology applications for edible oil refining process

[a]Polymer	[b]Membr. Class	Vegetable oil	Target(s)	[c]Achievement(s)	Drawback(s)	Reference
PI	Nonporous	Crude palm oil	Phosphorus removal	R_{Pho}=95 – 100%	High operating pressure (2–4 MPa) Hexane is used to dilute oil. Insignificant colour reduction.	[9]
PSU	UF (100KDa)	Soybean oil	FFA, soap and phosphorus removal	R_{FFA} = 34.39% R_{Pho}=73.37% R_{soap} = 85.81%	Incomplete removal of PLs and soap.	[14]
PVDF	UF (6000Da)	Soybean oil	Phosphorus removal	R_{Pho}=99.3%	Hexane is used to form miscella.	[7]
Cellulose	MF	Sunflower oil and rapeseed oil	FFA, soap and phosphorus removal	Results varied depending on the addition of H_3PO_4 and concentration of NaOH solution used and	Chemicals are needed to produce oil permeate of high quality. Fouling is severe in dead-end filtration.	[15]
PA	NF (Desal-5)	Model fatty acid solution	FFA removal	R_{FFA} = 75-84%	Methanol is required to extract FFA. Low solvent stability of membrane against alcohol.	[13]
Zirconia (Inorganic)	Ceramic UF (20nm)	Crude palm oil	Phosphorus and iron removal	R_{Pho}=78.1% R_{iron} = 59.7%	Incomplete rejection of PLs. No selectivity against FFA.	[17]

[a]PVDF = Polyvinylidene fluoride, PI = Polyimide, PSU=Polysulfone, PA = Polyamide
[b]MF=Microfiltration, UF=Ultrafitration, NF=Nanofiltration
[c]Pho = Phosphorus, FFA = Free fatty acid

MATERIALS AND METHODS

Materials

Commercial PVDF pellets (Kynar® 740) purchased from Arkema Inc., USA was used as main component in membrane formation. The reason of choosing this polymer in membrane preparation is mainly due to its excellent resistance against thermal and chemical. N-methyl-2-pyrrolidone (NMP) and ethylene glycol (EG) bought from Merck were used as solvent and additive respectively during dope solution preparation. Other chemicals used in this study for CPO refining process were purchased in analytical-grade and used as received without further treatment.

Dope solution preparation and membrane fabrication

Table 2 shows the dope formulation and spinning conditions of all hollow fiber PVDF membranes used in this study. During spinning process, all the parameters were kept constant, except the windup drum speed as mentioned in the table. After completing the spinning process, all membranes were required to keep in water bath for a day (to remove residual solvent) before subjecting to a post-treatment process using ethanol aqueous solution. The details on hollow fiber spinning process can be found on our previous research work [16].

Table 2: Dope formulation and spinning conditions of membranes used in this study

Membrane	**14 PVDF**	**18 PVDF**
Dope formulation (wt%)	14%PVDF 80%NMP 6% EG	18%PVDF 76%NMP 6% EG
Spinning conditions		
Bore fluid composition	Water	Water
Bore fluid rate (ml/min)	1.8	1.8
External coagulant	Water	Water
Coagulant temperature (^oC)	27	27
Air gap (mm)	100	100
Windup drum speed (cm/s)	15.7	13.2

Membrane CPO refining system

Degumming and deacidification of CPO were carried out simultaneously using a lab-scale membrane refining system. Prior to the refining process, a certain amount of phosphoric acid (80-85% conc.) or sodium hydroxide (5N) aqueous solution was added to eliminate PLs or FFA of CPO. The reaction process was performed under vigorous stirring at 85^{o}C for 50 min before it was ready for refining. In order to minimize membrane fouling effect, a conventional oil screening with spacing 1µm × 1µm was used to filter part of the soft matters formed before the neutralized palm oil (NPO) was fed into stainless steel membrane permeation cell of 1050 mL capacity. A U-tube shaped hollow fiber module which consisted of 60 fibers in 30 cm long (equivalent to 735 cm^2 effective area) was housed within the cell. The temperature of NPO within the cell was maintained at 50^{o}C (±1^{o}C) by immersing the housing into a water bath in which the temperature was controlled using multi-purpose immersion coiled heater (Model 830-S1, Protech Electronic). Meanwhile, the operating pressure for membrane refining process was maintained at desired value using pure nitrogen gas. All the experiments were dead end filtration and the quality of the refined oil was evaluated with respect to phosphorus, FFA and soap removal by collecting permeate from the downstream side of the cell through ½" stainless-steel tubing.

To measure oil flux, J (kg/m^2.h) achieved by each type of membranes, the following equation was employed.

$$J = \frac{Q}{At} \qquad (1)$$

where Q is quantity of permeate (kg), A is effective membrane area (m^2) and t is time to obtain the quantity of Q (h). The quality of permeate collected was assessed based on the rejection of respective compound as expressed in Eq. (2).

$$R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (2)$$

where C_p and C_f are the content of FFA/soap/phosphorus in permeate and feed, respectively.

Characterization on membrane structural morphology

The membrane cross-sectional morphology and outer surface was examined using field emission scanning electron microscope (FESEM, JEOL JSM-6701F). Prior to analysis, a piece of hollow fiber was immersed in liquid nitrogen and fractured carefully in order to create a perfect cross section. Outer top surface was observed at magnification of 25,000 × and the membrane average pore diameter was determined based on the image captured. As polymeric membrane was non-conductive, they were required to be coated with gold element using auto fine coater (JEOL JFC-1600) in order to provide shape image.

Analytical method of samples

Free fatty acid, phosphorus, peroxide value and soap contents in the oil samples were determined using American Oil Chemists' Society (AOCS) method - Cd 3d-63, Ca 12-55, Cd 8b-90 and Cc 17-95, respectively.

RESULTS AND DISCUSSION

Stability of CPO

Free fatty acid and peroxide value are two important parameters to determine the quality of crude palm oil. Owing to the enzyme action which hydrolyses ester bond in lipids after oilseed has been harvested [2], the content of FFA and PV of CPO would vary from day to day. Figure 1 shows the stability of CPO as a function of day with respect to FFA content and PV. As can be seen, FFA content and PV demonstrated increasing tendency in the studied period of 14 days regardless of the storing condition. Keeping the CPO under cold environment however was found to be able to slow down the values of both parameters. Results indicated that the final values of FFA and PV for CPO stored at 8°C were relatively lower compared with CPO stored at room condition. Cold-stored CPO showed only 4.40% FFA and 0.84% PV in comparison to 5.17% FFA and 2.05% PV of CPO stored at 25°C at day of 14. In order to minimize increases in FFA and PV, industrial oil refining processes are generally conducted soon after harvest. Nevertheless, due to the difficulty to obtain fresh CPO every day from oil refining plant for this research work, the sample of CPO was therefore kept at cold environment to minimize the change in its properties [17].

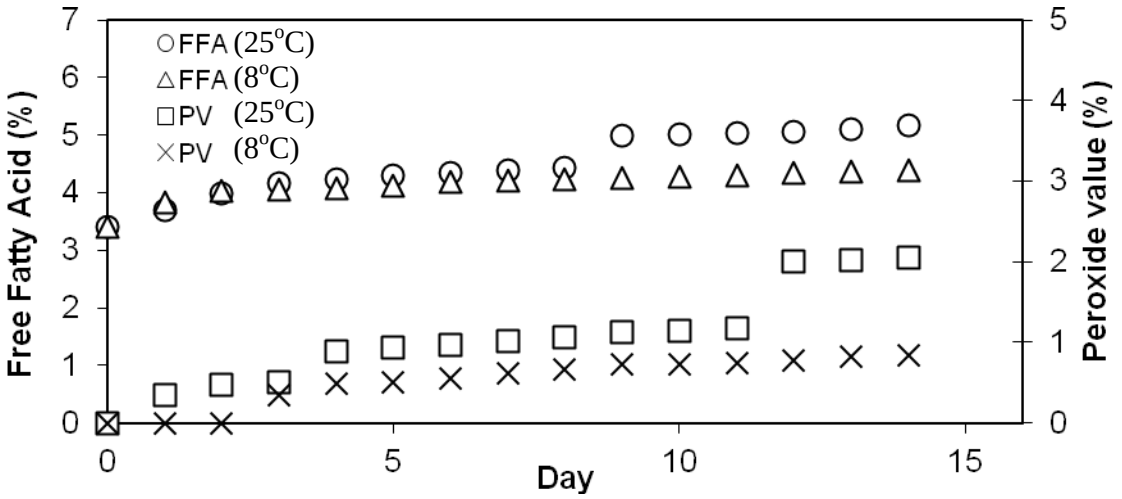

Fig. 1: The stability of CPO with respect to FFA (○ at 25°C; Δ at 8°C) and PV (□ at 25°C; × at 8°C) as a function of day

Membrane properties

Figure 2 presents the permeate flux profile of PVDF membranes operated at 2 bar and 50°C using crude palm oil without any pretreatment process. As can be clearly seen, both types of PVDF membranes suffered significant flux decline when they were used for oil filtration process. The initial flux of 14PVDF membrane was dropped sharply from 4.6 to 2.4 kg/m^2.h while 18PVDF membrane from 3.55 to 2.07 kg/m^2.h before they achieved stable oil flux at 180 min. Although the refining process was conducted at different conditions, significant flux deterioration was also reported by Pioch et al. [15] when they investigated the performance of commercial MF membranes in the sunflower and rapeseed oil refining process. The difference in the oil flux of membranes prepared was mainly caused by the use of different polymer concentration during dope preparation. It is found that the higher the polymer concentration, the

lower the oil permeability of membrane which can be strongly linked to the slower solvent and non solvent exchange rate during phase inversion process.

Figure 3 shows the FESEM pictures of PVDF membranes studied. As can be seen, there was a significant number of membrane pores existed on the outer surface of 14PVDF compared with 18PVDF membrane under the same magnification of 25,000×. Based on these image captured the average pore diameters of 14PVDF and 18PVDF membranes were estimated to be approximately 37.5nm and 24nm, respectively. The estimated pore sizes of membranes were also in good agreement with the results shown in Figure 2 in which the smaller the pore size, the higher the oil permeability of membrane, owing to a lower resistance for oil molecules to permeate.

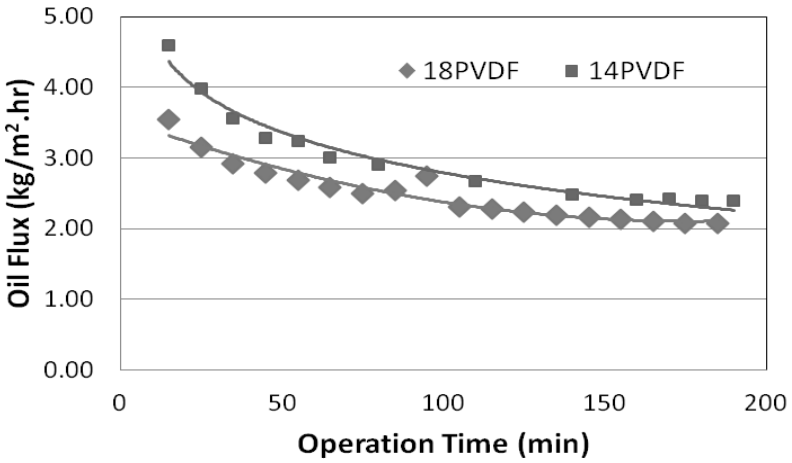

Fig. 2: Oil flux profile of membranes as a function of time

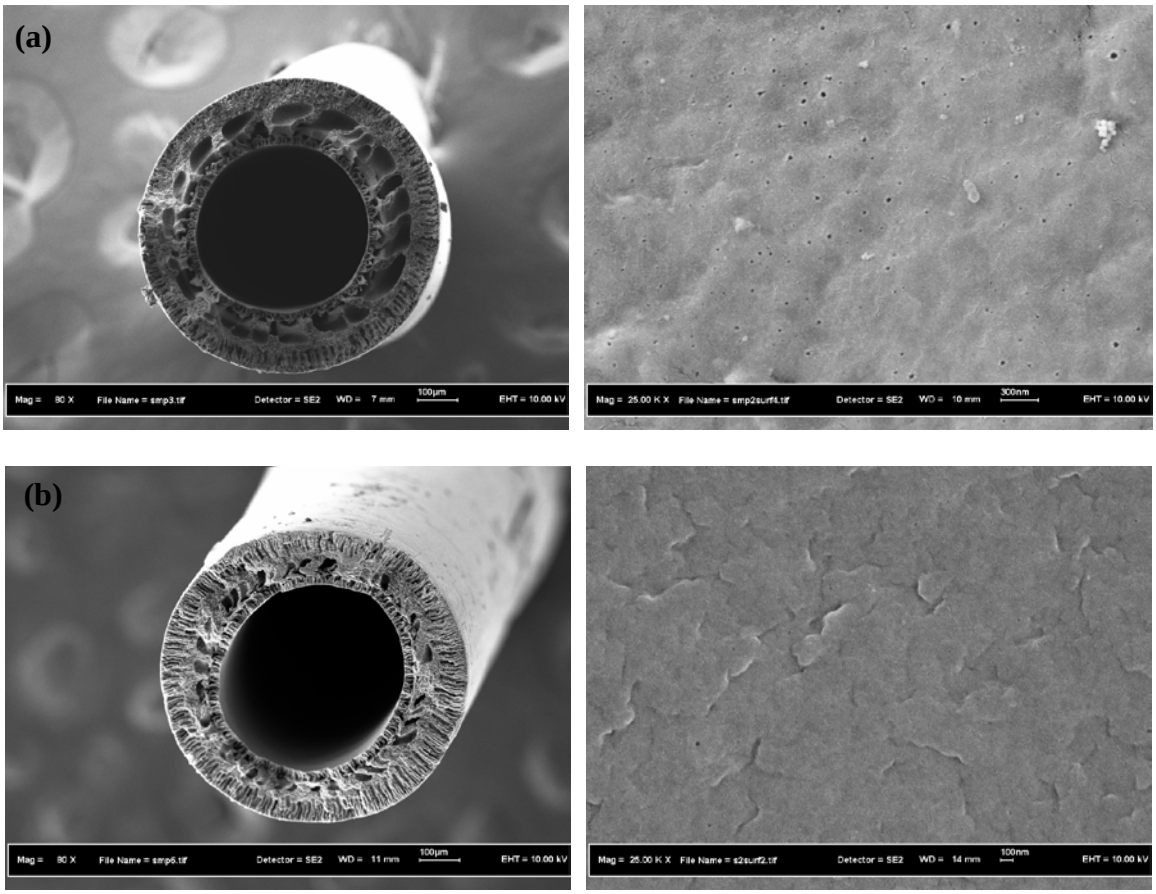

Fig. 3: The overall cross section (left, 80×) and outer surface (right, 25,000×) of (a) 14PVDF and (b) 18PVDF membranes.

Membrane CPO refining without the use of chemicals

In order to better understand the capability of membrane itself in removing PL and FFA from CPO, attempts have been made to refine CPO using in-house made membranes in the absence of chemicals. Table 3 shows the results obtained from membrane CPO refining without the use of H_3PO_4 and NaOH. It is found that membrane pore size played an important role in separating PLs from the oil solution. 18PVDF membrane which having smaller pore size demonstrated up to 93% rejection of phosphorus compared with 80% achieved using 14PVDF membrane. It is known that the MW of PL is very close to neutral triglycerides, but the significant size of the PL mixed micelles provides synergistic effect during membrane separation process, making it highly rejected by membrane [18].

With respect to FFA reduction, PVDF membranes were found to have little role in retaining FFA molecules. Both membranes showed less than 10% FFA rejection. Given the fact that the molecular size of FFA (<300 Da) is much smaller than that of triglycerides (~800 Da), FFA in principle is impossible to be removed by membranes. Previous research work also showed that even with the use of dense structured membrane, FFA would still permeate preferentially compared to triglycerides, resulting in negative rejection of FFA [2].

In addition to FFA and phosphorus, peroxide value was also taken into consideration during refining process because this value was important to assess the degree of oxidation for the oil samples studied [19]. Since the oil samples used were kept in cold condition and disposed after 2 weeks, the change in PV was insignificant as only trace amount of oxidized oil was reported in this current work.

Table 3: Permeate quality of membrane CPO refining without the use of chemicals

Membrane	[a]FFA			[a]Phosphorus			[a]PV		
	F (%)	P (%)	R (%)	F (ppm)	P (ppm)	R (%)	F (ppm)	P (ppm)	R (%)
14PVDF	[c]3.87	3.58	7.49	18.39	3.70	79.88	Trace	–	–
18PVDF	3.42	3.12	8.77	26.36	1.91	92.75	Trace	–	–

[a] F= Feed, P=Permeate and R=Rejection

Membrane CPO refining with the use of H_3PO_4

The main purpose of adding H_3PO_4 into crude palm oil is to coagulate PL molecules and sequestrate metals present in oil so as these impurities can be easily separated during refining process. If PLs are not removed, triglyceride oil will undergo undue darkening during deodorization process at high operating temperature.

In this section, the performances of PVDF membranes were studied in the presence of H_3PO_4 and the quality of refined oil produced are shown in Table 4. It can be seen that the use of H_3PO_4 during refining played no role in improving oil quality. Compared to refining process without addition of chemicals, the percentage of FFA reduction in the presence of H_3PO_4 remained almost the same while PL separation rate decreased considerably. The significant change of phosphorus separation can be attributed to the increased phosphorus content in the oil upon addition of H_3PO_4. This as a consequence affected badly the performance of the membranes, producing permeate of significant content of phosphorus.

Table 4: Permeate quality of membrane CPO refining with the use of H_3PO_4

Membrane	FFA			Phosphorus			PV		
	F (%)	P (%)	R (%)	F (ppm)	P (ppm)	R (%)	F (ppm)	P (ppm)	R (%)
14PVDF	3.33	3.10	6.91	127.00	70.09	44.96	Trace	–	–
18PVDF	3.33	3.10	6.91	127.33	59.25	53.47	Trace	–	–

Simultaneous degumming and deacidification of CPO using PVDF membranes

In order to have a complete FFA elimination, the use of NaOH to neutralize FFA is necessary, though soap and oil loss are happened as a result of neutralization. It has been evidenced in the previous section that our in-house made membranes have the potential to produce permeate of low phosphorus content in the absence of chemicals, we therefore would like to investigate the optimum dosage of NaOH solution required to reduce FFA in the absence of H_3PO_4. In order to assess the quality of the oil refined, the following concentration limits of industrial standard for neutralized palm oil were used:
FFA less than 0.15%
Soap less than 20ppm
Phosphorus close to nil

Table 5 tabulates the quality of oil refined by PVDF membranes at different NaOH quantity. The optimal quantity of NaOH solution needed for conventional chemical refining process (i.e. 100% shown in the table) was experimentally determined through titration methods and it varied depending on the content of FFA in the CPO. By reducing the dosage of NaOH solution used, we would like to know if the PVDF membranes studied could still perform in terms of reducing FFA content to meet the industrial concentration limits under reduced dosage of NaOH solution. It must be pointed out that the addition of NaOH during refining process would produce soapstock as by-product following a neutralization of FFA as illustrated in Figure 4. The soapstock produced is generally known to be able to trap gum, oil and trace metals, forming a complex soft matters. Due to this point, additional quality assessment was required to determine the content of soap in the oil refined using membranes.

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In this study, it is reported that the highest separation rates of soap and PL were achieved in the case of 100% NaOH usage, followed by 80% and 60% NaOH. As soap was appeared as softmatters during refining process, it was generally considered that the separation of soap was based on the sieving mechanism. Comparing between 14PVDF and 18PVDF membranes, it is realised that membranes having smaller pore size demonstrated higher separation efficiency to produce oil permeate of slightly better quality with respect to its phosphorus and soap content. Based on the results obtained, one may also conclude that the quality of refined oils was very similar either by centrifugation (standard procedure) or membrane technology.

On that other hand, it is found that the amount of NaOH aqueous solution added has a very significant impact on the FFA content of refined oils. The results showed that
the greater the amount of NaOH added during refining process, the lower the FFA content in the oil permeate and the higher the quality of refined oil produced. Based on these results, it is confirmed that complete neutralization could only be achieved provided there were sufficient NaOH to neutralize the FFA in the oil. The results also indicated that the membranes studied played insignificant role in the reduction of FFA content. Despite membranes showing little contribution to FFA reduction in the absence of NaOH solution, it is still possible to make full use of membrane technology through embedding compatible FFA absorbents into membrane matrix. This area of study however requires further investigations.

Table 5: Permeate quality of membrane CPO refining with the use of different amounts of NaOH

Membrane	**FFA**			**Soap**			**PV**		**Phosphorous**		
	F (%)	**P (%)**	**R (%)**	**F (ppm)**	**P (ppm)**	**R (%)**	**F (%)**	**P (%)**	**F (ppm)**	**P (ppm)**	**R (%)**
100% NaOH											
14PVDF	3.87	0.21	94.57	2663	0.00	100	Nil	–	17.19	0.08	99.59
18PVDF	3.87	0.15	96.12	2663	0.00	100	Nil	–	17.19	0.12	99.30
80% NaOH											
14PVDF	3.63	0.25	93.11	749.9	13.80	98.2	Nil	–	13.28	0.33	97.52
18PVDF	3.63	0.26	92.84	935.7	0.00	100	Nil	–	19.24	0.20	98.96
60% NaOH											
14PVDF	4.00	0.77	80.75	2363	83.23	96.48	Nil	–	16.64	0.41	97.54
18PVDF	4.00	0.85	78.75	2363	55.54	97.65	Nil	–	16.64	0.61	96.33

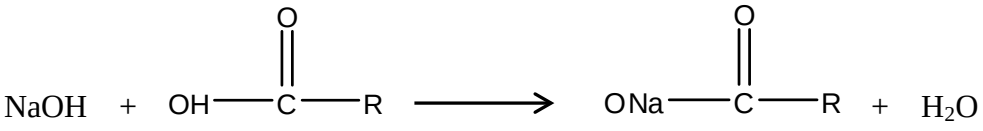

Fig. 4: The formation of soapstock (weak base) from the reaction between sodium hydroxide and free fatty acid.

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CONCLUSIONS

In this study, two types of in-house made PVDF hollow fiber membranes were used to refine CPO under different refining process conditions. The results obtained from experimental studies have led to the following conclusions:

a) 18PVDF membrane demonstrated up to 93% phosphorus rejection compared to 80% in 14PVDF membrane in the refining process without the use of chemicals. The high rejection rate of phosphorus can be attributed to the significant difference between the pore size of 18PVDF membrane and molecular size of PLs. The rejection of FFA on the other hand was found to be less than 10% and this was mainly due to very small MW of FFA in comparison to PLs.
b) Addition of H_3PO_4 for degumming process showed no improvement on the refined oil quality. It is found that the content of phosphorus in the CPO was increased considerably upon addition of H_3PO_4 and this had led to a decrease in phosphorus rejection of both membranes from 80–93% (in the absence of H_3PO_4) to 45–53%. The results indicated that membranes' good performance in PL removal was badly affected when H_3PO_4 was used during refining process.
c) It is found that the higher the amount of NaOH used, the better the quality of oil produced. Excellent oil quality was able to achieve when optimized NaOH amount was used. Any reduction from that optimized amount was reported to produce oil containing relatively high FFA and failed to meet the standard for subsequent refining process.

Based on the results obtained from the experimental studies, it is showed that in the absence of H_3PO_4 to assist degumming process, PVDF membranes were still able to demonstrate excellent performances in the separation of FFA and PLs from the CPO provided there was sufficient NaOH amount to neutralize FFAs existed. Besides cutting down the cost of chemicals used (by eliminating the usage of H_3PO_4), membrane CPO refining also offered advantages of minimizing water usage and generating no wastewater from food processing plant.

FUTURE WORKS

In the following studies, we will investigate the possibility of embedding FFA absorbents into the PVDF membranes to create synergistic effects to eliminate FFA and PLs simultaneously in the absence of chemicals. The period of membrane refining process will also be prolonged so as we are able to assess membrane fouling problem and identify suitable cleaning method for flux recovery. To our best knowledge, all of the scope has yet to be reported in the literature. It is worthy of investigation.

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