Simultaneous degumming and deacidification of crude palm oil using mixed matrix PVDF membrane

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Abstract. The research work aimed to investigate the compatibility of polyvinylidene difluoride (PVDF) membrane embedded with various inorganic adsorbents for producing a mixed matrix membrane (MMM) and to examine the capability of mixed matrix PVDF membrane (PVDF-MMM) for simultaneous degumming and deacidification of crude palm oil (CPO). Four different adsorbent were tested which includes calcium silicate (CaS), magnesium silicate (MagS), ZSM-zeolite (ZSM) and activated carbon (AC). The in-house made PVDF-MMM was fabricated according to the dry-jet wet spinning method. The performances of these PVDF-MMMs were assessed with respect to the removals of phosphorus, FFA and colour. Based on finding showed that the combination of 18PVDF embedded with 3 wt% MagS showed the most compatible polymer-inorganic hybrid MMM to perform pre-treatment of CPO. Increasing the MagS concentration from 3 to 8 wt% in the polymer matrix recorded the highest removals of FFA at 16.51 %, phospholipid at 93.31 % and colour at 18.8 %, respectively. Nevertheless, high amount of MagS added to the polymer matrix affected the spinnability and reproducibility performance of MMM. Future work, surface modifications of inorganic adsorbent can be evaluated to facilitate good dispersion of filler in polymer matrix during membrane fabrication to maintain good membrane reproducibility.

1. Introduction
The production of crude palm oil (CPO) at oil mill processing usually contains variable amounts of minor components such as free fatty acids (FFA), partial acylglycerols, phosphatides, sterols, tocopherols, tocotrienols, hydrocarbons, pigments, traces of pesticides, dioxins, metal ions and oxidation by-products. The CPO must undergo a refining process to remove all unwanted compounds so that the final refined oil is of good quality, stable and safe for human consumption. From an industrial perspective, the goal of refining is to convert the crude oil into a high quality edible oil by reducing unwanted impurities to the desired level as efficiently as possible. This means that, losses of desirable components should be kept to a minimum and cost effective [1]. Two refining methods commonly used at palm oil refinery are the physical refining process for most refined palm oil products and the chemical refining process for more specialized products according to customer requirements.

Degumming and deacidification are very important steps in the palm oil refining process. The main objective of the degumming process is to remove the gums or phosphatides in CPO. The gums must be
removed at an early stage of refining to avoid high refining losses as they are emulsifying and thermally unstable that burns at high deodorization temperatures. In addition, the presence of gums contributes to off-flavor and poor oxidation stability as phosphatides coordinate with metal ions such as copper, iron, calcium and magnesium which are catalysts for oil oxidation. There are 2 types of phospholipids (PLs), namely hydratable and non-hydratable. The hydratable phospholipid can be easily removed by adding water and then centrifuging. This process is called water degumming. The non-hydratable phospholipids associated with calcium and magnesium salt need to be converted to hydratable ones by acid treatment with phosphoric acid or citric acid [2].

Deacidification is the process of removing FFA in CPO. FFA is undesirable because it is one of the pro-oxidant compounds that reduce oxidative stability, increase the acidity of the oil and lead to the formation of off-flavors in the refined end products. In the physical refining process, deacidification was carried out at high vacuum-steam distillation and deodorization temperatures between 260 – 265 °C to strip the FFA into volatile odorous compounds and remove them in the form of palm fatty acid distillate. In the chemical refining process, deacidification was carried out with sodium hydroxide (NaOH) to neutralize and remove the FFA in the form of soapstock. The FFA content in CPO determines the amount of NaOH to be added for the neutralization process. Any residual soapstock is removed by adding hot water and then centrifuging. The remaining FFA in the neutralized bleached palm oil is further removed in the final deodorization stage at lower temperatures between 220 – 240 °C [3].

The use of phosphoric acid and caustic soda for the degumming and neutralization process had become an environmental and safety issue due to their disposal. Large amounts of wastewater generated during the deacidification process require costly treatment for soapstock. As a result, both capital and energy costs are high [4]. In physical refining, the elimination of the neutralization step has the advantage of reducing the loss of neutral oil and simplifying process operation. Nevertheless, high operating costs (steam, electricity and water) are required to maintain the operation as steam and operating temperatures are high [5, 6].

Membrane technology is a mature industry that has been successfully applied in various food industries for separation of undesirable compounds, water and waste-water treatments as well as gas separation. It offers a huge potential that worth to explore in palm oil industry to harvest the benefits towards green and mild processing technology to eliminate the use of chemical, low energy consumption as well as retention of nutrients [7]. Köseoglu and Engelgau had reported on membrane applications and research in the edible oil industry since 1990 [8]. Fast forward to the present, one can see the increasing number of relevant research works in refining process in particular in the applications of degumming and deacidification [9–12]. Previous studies have reported that ultrafiltration (UF) membrane can be very effective (depending on the pore size selected) in separating phospholipid from vegetable oils without adding any chemical during degumming process [3,13–15]. Other than pressure-driven filtration membrane, polyphenylsulfone hollow fiber (HF) membrane for CPO deacidification through membrane contactor was reported by Othman et al. (2017) to extract the FFA in CPO using NaOH as liquid extractant without soap formation [16,17]. Azmi et al. (2016) reported on PVA-crosslinked PVDF membrane to improve the surface affinity toward FFA for direct deacidification of CPO [18].

Our previous studies revealed that membrane-based separation technology using PVDF hollow fiber membranes was a promising alternative for degumming of CPO with phosphorus content in permeate below 2 ppm [3]. However, its effectiveness in removing FFA was not promising due to small differences in molecular weight of major component of CPO (triglycerides ~900 Dalton) and FFA (~300 Dalton) [19]. Mixed matrix membrane (MMM) was one of possible approaches to improve the separation properties of invented PVDF membrane. It is a polymer–inorganic hybrid membrane that may offer a synergistic effects rendered by both polymeric matrix and inorganic fillers such as good selectivity and permeability, superior mechanical strength and high resistant to chemical and temperature [20].

The present research work aimed to investigate the compatibility of in-house made PVDF mixed matrix membrane (MMM) embedded with various inorganic adsorbents and to examine the of PVDF-
MMMs for simultaneous degumming and deacidification of CPO in removing the phospholipids (PLs - measured by phosphorus content) and free fatty acid (FFA).

2. Materials and Methods

2.1. Materials
Crude palm oil (CPO) was obtained from Sime Darby Oils Langat Refinery located at Telok Panglima Garang, Selangor. Table 1 shows the specifications of CPO according to Malaysian Standard MS814:2007. The main membrane raw material of polyvinylidene fluoride (PVDF) pellets (Kynar® 740) was purchased from Arkema Inc., USA. Whereas N-methyl-2-pyrrolidone (NMP) and ethylene glycol (EG) were bought from Merck. The inorganic absorbents to be embedded into PVDF membranes consisted of magnesium silicate or trade name known as Magnesol (MagS) obtained from Dallas Group, activated carbon (AC) obtained from SYSTERM®, zeolite (ZMS) and calcium silicate (CaS) which both obtained from Sigma Aldrich. All chemicals used in this work were received without further treatment.

| Identity Characteristics | Observed Range       | Mean ± Standard Devition |
|--------------------------|----------------------|--------------------------|
| Apparent density, kg/L at 50 °C | 0.8889 – 0.8896 | 0.00892 ± 0.0002 |
| Refractive index at 50 °C | 1.4521 – 1.4541 | 1.4533 ± 0.0003 |
| Saponification value, mg KOH/g oil | 194 - 205 | 199 ± 2.4 |
| Unsaponifiable matter, % | 0.19 – 0.44 | 0.32 ± 0.066 |
| Iodine Value (Wjjs) | 50.4 – 53.7 | 52 ± 0.66 |
| Slip Melting Point, °C | 33.8 – 39.2 | 36.7 ± 0.84 |
| Total carotenoid (as β-carotene), mg/kg | 474 - 689 | 581 ± 45.5 |

2.2. Formulation of Dope Solution for Mixed Matrix Membrane
PVDF pellet was dried at 100 °C for 5 hours to remove the moisture contents. The dried PVDF was gradually added to a combination of NMP, EG and inorganic absorbent of various properties (MagS, AC, ZSM and CaS) in the reaction flask and mixed thoroughly under constant mechanical stirring at 60 °C. It took at least 1 day to produce a homogenous solution in order to ensure the PVDF-MMM was completely dissolved in the solvent. Finally, the prepared dope solution was degassed to remove any micro-bubbles that might exist before spinning. Table 2 listed all the dope solutions made for fabrication of hollow fiber PVDF-MMMs.

| Membrane       | Polymer | Dope Formulation (%) | Solvent | Additive | Adsorbent |
|----------------|---------|----------------------|---------|----------|-----------|
| 18PVDF+3CaS    | 18% PVDF| 73% NMP              | 6% EG   | 3% CaS   |
| 18PVDF+3AC     | 18% PVDF| 73% NMP              | 6% EG   | 3% AC    |
| 18PVDF+3ZSM    | 18% PVDF| 73% NMP              | 6% EG   | 3% ZSM   |
| 18PVDF+3MagS   | 18% PVDF| 73% NMP              | 6% EG   | 3% MagS  |
| 18PVDF+5MagS   | 18% PVDF| 71% NMP              | 6% EG   | 5% MagS  |
| 18PVDF+8MagS   | 18% PVDF| 68% NMP              | 6% EG   | 8% MagS  |

2.3. Fabrication of Hollow Fiber Mixed Matrix Membrane
The hollow fiber membranes were fabricated using a technique known as dry-jet wet spinning. Once the spinning dope and the bore fluid (water) met at the tip of the spinneret with air gap of 10cm, the hollow fiber membrane was produced simultaneously and transferred directly into an external coagulation bath (water). After that, the fibers went through a washing/treatment bath before they being gathered by a
wind-up drum. The as-spun membranes were kept in a water bath at room temperature for 1 day, post-treated with ethanol solution to prevent shrinkage and lastly air-dried at room temperature before being used to make a test module. The hollow fiber membranes were potted into bundles of 60 fibers with a length of 25 cm into the U shape test module before ready for testing.

2.4. Mixed Matrix Membranes Performance for Pre-treatment of Crude Palm Oil

The membrane pre-treatment of CPO was set in a simple dead end filtration mode as shown in figure 1. CPO was semi-solid at room temperature. It must be heated at 60 °C to keep it in a liquid state before fed into a MMM processing module. The pre-treatment of CPO was conducted under pressure-driven membrane filtration operated at 2 bar for 1 hour to obtain a sufficient amount of permeate fraction for sample analysis. The performances of these MMMs were evaluated based on the percentage removals of FFA, phosphorus and colour of pre-treated CPO (permeate) as compared to initial CPO (feed).

![Figure 1. Experimental setup for CPO membrane pre-treatment system.](image)

2.5. Analytical Methods

The analysis of feed CPO and permeate (pre-treated CPO) with respect to phosphorus, FFA and colour were determined in accordance to American Oil Chemists’ Society (AOCS) method using AOCS method of Ca 12-55, Ca 5a-40 and Cc 13e-92, respectively.

3. Results and Discussion

Table 3 shows the performances of MMM embedded with four different adsorbents for pre-treatment of CPO. It can be observed that 18PVDF+3MagS MMM exhibited the highest FFA removal among the MMMs tested which recorded at 8.18 %. Besides, it was also able to eliminate more than 90 % phosphorus with 13.3 % colour removal in permeate sample. 18PVDF+3CaS membrane showed slight reduction in FFA (7.8 %), followed by 18PVDF+3AC (6.4 %) and 18PVDF+3ZSM (0 %). Although the efficiency of FFA removal was reduced, the MMMs embedded with CaS, ZSM and AC were able to maintain a promising phosphorus removal (at least 87.3 %), achieving no more than 2 ppm phosphorus content in the permeate sample similar to the conventional phosphoric acid degumming.

PLs in nature had both hydrophilic and hydrophobic functional groups [8,21]. Although it had almost similar molecular weight (700 Dalton) with triglycerides (900 Dalton) [22], it can form a reverse micelle (MW of 20,000 Da) in a non-aqueous environment due to its surfactant properties [8,12]. The large size of the PLs mixed micelles has a synergistic effect during the membrane separation process, causing it to be significantly rejected by the membrane [21]. The significant challenge of using MMM for removing FFA is the possibility of the internal channel blockage and/or active surface coverage of the adsorbent by polymer, reducing the effective area of adsorption which leads to lower FFA rejection.
Increasing the range. All solutions which affected the filtration of CPO. Surface modification of inorganic adsorbent can be further evaluated to improve dispersion and severe agglomeration of MagS in the dope solution as a result of incompatibility between PVDF membrane matrix and inorganic filler. As a consequence, it affected the spinnability and reproducibility of MMM membranes fabricated via a dry-jet wet spinning method. Among four different adsorbent tested for fabrication of PVDF-MMMs, the combination of 18PVDF+3MagS showed the most compatible to perform a simultaneous degumming and deacidification of CPO with 8.16 % FFA removal, eliminated up to 90.28 % phosphorus with 13.3 % colour has been reduced simultaneously. Increasing the amount of MagS embedded into the PVDF membrane matrix had further improved the removal of FFA at 16.51 %, phosphorus up to 93.31 % and colour up to 18.8 %, respectively as recorded by 18PVDF+8MagS MMM. Unfortunately, high amount of MagS added into polymer matrix unable to sustain the membrane reproducibility due to poor dispersion and severe agglomeration of MagS in the dope solution which affected the filtration performance of CPO. Surface modification of inorganic adsorbent can be further evaluated to improve the dispersion of MagS in the PVDF polymer matrix at high concentration of inorganic filler.

Table 3. The performances of mixed matrix PVDF membranes embedded with different adsorbents for pre-treatment of CPO.

| Mixed Matrix Membrane | FFA (%) | Permeate (%) | Rej. (%) | Phosphorus | Permeate (ppm) | Rej. (%) | Colour (5R+Y) |
|-----------------------|---------|--------------|---------|------------|----------------|---------|--------------|
| 18PVDF+3CaS          | 3.34    | 3.10         | 7.46    | 10.50      | 1.09           | 89.62   | 165          | 135 | 18.2 |
| 18PVDF+3MagS         | 3.79    | 3.48         | 8.18    | 14.30      | 1.39           | 90.28   | 158          | 137 | 13.3 |
| 18PVDF+3ZSM          | 3.79    | 3.79         | 0.00    | 14.24      | 1.67           | 88.27   | 158          | 138 | 12.6 |
| 18PVDF+3AC           | 3.34    | 3.12         | 6.31    | 10.50      | 1.34           | 87.33   | 160          | 138 | 13.7 |

Magnesol in fact very ideal for use as adsorbent in improving the shelf life of frying oil. Official data from the producer have confirmed that Magnesol can remove both solid and dissolved impurities from the oil, owing to its acid and basic adsorptive sites which allow promising removal of polar compounds including FFA. Table 4 compares the performances of the PVDF membrane embedded with different weight content of magnesium silicate (MagS) to enhance the deacidification of CPO. Increasing the amount of MagS in the membrane matrix was able to further increased the FFA removal in the permeate sample from 8.18 % (18PVDF+3MagS) to 16.51 % (18PVDF+8MagS), respectively. It was mainly due to the increased active surface of the adsorbent which improves the adsorption capacity of PVDF-MMM. It must be noted that the promising rejection of phosphorus was not negatively affected with increasing content of MagS in membrane. All PVDF-MMMs modules were reported to remove at least 90 % phosphorus, producing a permeate containing between 1.13 and 1.39 ppm phosphorus.

Nevertheless, it must be pointed out that some issue been faced when high amount of MagS was added into polymer matrix. Severe agglomeration and poor dispersion of MagS was encountered at the bottom of membrane dope solution as a result of incompatibility between PVDF membrane matrix and inorganic filler. As a consequence, it affected the spinnability and reproducibility of MMM performances especially in removing the FFA.

Table 4. The performances of mixed matrix PVDF membranes embedded with different amount of MagS for pre-treatment of CPO.

| Mixed Matrix Membrane | FFA (%) | Permeate (%) | Rej. (%) | Phosphorus | Permeate (ppm) | Rej. (%) | Colour (5R+Y) |
|-----------------------|---------|--------------|---------|------------|----------------|---------|--------------|
| 18PVDF+3MagS          | 3.79    | 3.48         | 8.18    | 14.30      | 1.39           | 90.28   | 158          | 137 | 13.3 |
| 18PVDF+5MagS          | 3.74    | 3.42         | 8.56    | 14.54      | 1.18           | 91.88   | 158          | 148 | 6.3  |
| 18PVDF+8MagS          | 4.18    | 3.49         | 16.51   | 16.90      | 1.13           | 93.31   | 170          | 138 | 18.8 |

4. Conclusion
Mixed matrix membranes embedded with various absorbents successfully fabricated via a dry-jet wet spinning method. Among four different adsorbent tested for fabrication of PVDF-MMMs, the combination of 18PVDF+3MagS showed the most compatible to perform a simultaneous degumming and deacidification of CPO with 8.16 % FFA removal, eliminated up to 90.28 % phosphorus with 13.3 % colour has been reduced simultaneously. Increasing the amount of MagS embedded into the PVDF membrane matrix had further improved the removal of FFA at 16.51 %, phosphorus up to 93.31 % and colour up to 18.8 %, respectively as recorded by 18PVDF+8MagS MMM. Unfortunately, high amount of MagS added into polymer matrix unable to sustain the membrane reproducibility due to poor dispersion and severe agglomeration of MagS in the dope solution which affected the filtration performance of CPO. Surface modification of inorganic adsorbent can be further evaluated to improve the dispersion of MagS in the PVDF polymer matrix at high concentration of inorganic filler.
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References
[1] Gibon V, Greyt W and Kellens M 2007 Eur. J. Lipid Sci. Tech. 109 315–35
[2] Othman N H, Latip R A, Yusoff M S A, Ismail A F, Lau W J, Ng B C, Abdullah M S and Saidin M A R, inventors. Sime Darby Malaysia Berhad, assignee. A Process for Degumming of Crude Palm Oil. World Intellectual Property Organization WO 2014/058294 A1. 2014-4-17
[3] Othman N H, Noor A M, Yusoff M S A, Ismail A F, Goh P S and Lau W J. 2016 Membrane Technology for Water and Wastewater Treatment, Energy and Environment Vol 3 ed AF Ismail and T Matsuura (London: CRC Press) chapter 5 pp 297–307
[4] Lai L L, Soheili K C and Artz W E 2008 J. Am. Oil Chem. Soc. 85, Issue 2, 189–96
[5] Destaillats F, Craft B D, Sandoz L and Nagy K 2012a Food Addit. and Contam. 1 29–37
[6] Destaillats F, Craft B D, Sandoz L and Nagy K 2012b Food Chem. 4 1391–8
[7] Cui Z F and Muralidhara H S 2010 Membr. Technol. 312
[8] Koseoglu S S and Engelgau D E 1990 J. Am. Oil Chem. Soc 4 239–49
[9] Raman L P, Cheryan M and Rajagopalan N 1996 J. Am. Oil. Chem. Soc. 73 219–24
[10] Pagliero C, Ochoa N, Marchese J and Mattea M 2004 J. Chem. Technol. Biotechnol. 79 148–52
[11] Manjula S and Subramani R 2009 Sep. Purif. Technol 66 223–8
[12] Iyuke S E., Ahmadun F and Majid R A 2004 J. Food Process Eng. 27 476–96
[13] Othman N H, Noor A M, Latip R A, Yusoff M S A, Ibrahim S, Ismail A F, Lau W J, Goh P S, Ng B C, Abdullah M S and Saidin M A R, inventors. Sime Darby Malaysia Berhad, assignee. A Membrane Pre-treatment System and Process for Producing Refined Oils and Fats. World Intellectual Property Organization WO 2015/053609 A1. 2015-4-16
[14] Koris E M 2006 Desalination 200 537–9
[15] Kim I C, Kim J H, Lee K H and Tak T M 2002 J. Membr. Sci. 205 113–23
[16] Othman N H, Noor A M, Yusoff M S A, Goh P S and Ismail A F 2017 J. Membr. Sci. Res. 3 291–5
[17] Othman N H, Noor A M, Yusoff M S A, Goh P S, Lau W J, Ng B C and Ismail A F 2017 Malays. J. Anal. Sci. 21 633–42
[18] Azmi R A, Goh P S, Ismail A F, Lau W J, Ng B C, Othman N H, Noor AM and Yusoff M S A 2015 J. Food Eng. 166 165–73
[19] Cheryan M 2005 Membr. Technol. 2 5–7
[20] Souza V C and Quadri M G N 2013 Braz. J. Chem. Eng. 4 683–700
[21] Gupta A K S, inventor. Lever Brothers Company, assignee. Process for Refining Crude Glyceride Oils by Membrane Filtration. United States Patent 4062882. 1977-12-13
[22] Ochoa N, Pagliero C, Marchese J and Mattea M 2001 Sep. Purif. Technol. 22 417–22