BIPHASIC CRUDE PALM OIL DECHLORINATION: EFFECT OF VOLUME RATIO AND CONCENTRATION OF SODIUM SILICATE TO HYDROXIDE ION DISTRIBUTION

ZULFA KURNIA UMANI HARI[1], SYAMSUL BAHARI ABDULLAH[1],
SAIDATUL SHIMA JAMARI[1], CHE RAHMAT CHE MAT[3]
AND MOHD SABRI MAHMUD [1, 2]

[1]*Faculty of Chemical and Process Engineering Technology,* [2]*Centre for Research in Advanced Fluid & Processes, Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia*
[3]*Malaysian Palm Oil Board, 6, Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor*

*Corresponding author: mohdsabri@ump.edu.my

ABSTRACT: Dechlorination of crude palm oil (CPO) to prevent toxic contaminant formation inspired studies of applying alkaline in its treatments. This paper reports distribution of hydroxide ion (OH^-) from sodium hydroxide (NaOH) and sodium silicate (SS) between aqueous solution and CPO under equilibrium systems to moderate its presence in CPO and minimize saponification. In this study, OH^- was determined through pH measurements, which also indicated sodium hydroxide (NaOH) presence. Filtered CPO was mixed with SS solution at room temperature in various volume ratios and SS concentrations under 800-rpm agitation before being settling down to form layers of liquids. The One-Factor-in-A-Time approach was used to optimize the ratio. Acid value test and GCMS analyses were used to determine free fatty acids. Calibration curve construction revealed 0.0818 of OH^- dissociation constant. SS solution could turn to acidic at 6.344×10^{-5} g/ml of concentration probably due to hydrated silica. Using 0.01 g/ml SS solution, volume ratios between CPO and SS solution spanning from 0.33 to 3 were all under alkaline conditions but decreasing OH^- concentration, where 2 liquid phases only appeared in the ratio of 2.33 and 3. Concentration of SS was then varied for the 2.33 volume ratio and a sigmoid trend of OH^- increase was evident. The McCabe-Thiele plot revealed hydroxide ion equilibrium below operating line suggesting its extraction impossibility to CPO.

ABSTRAK: Penyahklorinan minyak sawit mentah (MSM) bertujuan mencegah pembentukan bahan cemar toksik telah mendorong penggunaan alkali dalam rawatan minyak itu. Manuskrip ini melaporkan taburan ion hidroksida (OH^-) daripada sodium hidroksida dan sodium silikat (SS) antara larutan akueus dan MSM di bawah keadaan penampan untuk mengurangkan kehadirannya dalam MSM bagi mengelakkan pembentukan sabun. Dalam kajian ini, kepekatan OH^- ditentukan melalui pengukuran pH, yang juga merupakan petunjuk kepada kewujudan NaOH. MSM yang ditapis dicampur dengan larutan SS pada suhu bilik dalam pelbagai nisbah isipadu dan kepekatan di bawah pengadukan 800 rpm sebelum diendapkan untuk membentuk lapisan cecair. Pendekatan Satu-Faktor-Sekali telah digunakan untuk mengoptimakan nisbah tersebut. Ujian nilai asid dan analisis GCMS digunakan untuk menentukan kandungan asid lemak bebas. Penjanaan lengkung penentu-ukuran membolehkan pemalar pelepasan OH^- diperoleh iaitu 0.0818. Larutan SS boleh bertukar asid pada kepekatan 6.344×10^{-5} g/ml mungkin disebabkan silika yang terhidrasi. Dengan menggunakan larutan SS 0.01 g/ml, nisbah isipadu antara MSM dan larutan SS dari 0.33 ke 3 berkeadaan alkali dan menurun kepekatan hidroksida. 2 fasa cecair hanya wujud pada nisbah 2.33 dan 3. Kemudian kepekatan SS diubah-ubah untuk nisbah isipadi 2.33 itu

dan corak sigmoid hidroksida diperoleh. Plot McCabe-Thiele mendapati keseimbangan kepekatan hidroksida berada di bawah garisan operasi menunjukkan pengekstrakan adalah mustahil berlaku terhadap OH⁻ ke dalam MSM.

1 INTRODUCTION

Malaysian palm oil has been banned by European Union (EU) due to the issue of 3-monochloropropandiol (MCPD) ester and glycidyl esters. These two contaminants are carcinogenic. Thus, a requirement of 1.25-ppm and 1-ppm maxima are imposed respectively to enter their market. Many removal methods of the contaminants have been tested either in lab scale or industrial scale.

MCPD diesters are normally generated from triglycerides after their glycerol molecules have been attacked by chlorine or chloride in nucleophilic substitution reactions under acidic aqueous solution environment to form chloropropanols [1]. The production of 2-MCPD and 3-MCPD derivatives is in a five-atom cyclic carbocation intermediate mechanism or a three-member epoxide ring structure. Formation of MCPD fatty acid diester is usually by heating a mixture of triheptadecanoin and lindane (an organochlorine agent) and MCPD diester formation was found to be significant at 200°C and above, but not at temperatures between 100°C and 180°C. The observation could not be explained by any of the reported cation or glycidol mechanisms suggesting that under low moisture, high temperature conditions, 3-MCPD esters formation may have a new mechanism with chlorine. In this case, triglycerides and chlorine are probably precursors to the MCPD diester synthesis: cyclic acyloxonium or glycidyl ester 3-MCPD monoester and diester synthesis, beside acidity, catalyst and moisture [2].

Several efforts have been made by Malaysia Palm Oil Board (MPOB) to help local industries comply standard palm oil mill requirement such as cleaning palm oil fruits bunch before extraction [3-5], segregation of sterilizer condensate and empty fruit bunch streams from primary CPO production [6], liquid-liquid extraction with a polar solvent solution [7] and pre-treatment process using dechlorinating agent. Dechlorination of CPO is particularly a new approach as a result of a regulation implemented by MPOB in 2019 [8]. Enforcement of this regulation is however still pending because of the difficulty in getting a practical technique to conduct the dechlorination in mills as there are several forms of chlorine in CPO.

Currently available patent is by using magnesium silicate in CPO bleaching, which resulted in significant reduction of 3-MCPD ester in refined- bleached- deodorized palm oil in some refinery processes [2]. Magnesium chloride synthesized from the dechlorination reaction is water soluble. In general, reactions in an heterogenous system was usually deteriorated by mass transfer problems. In synthesis of a chemical process, liquid-liquid system is generally more practical and economical. CPO is currently washed by using raw water, but the supplied general raw water usually contains chlorine for killing germs and microbes. Thus, an additional dechlorination system must be applied to treat the raw water before the CPO washing. The amount of the treated water used to remove chlorine in CPO is a lot because of the solubility issue of organic chloride. Therefore, an alternative liquid-liquid system is in need to reduce the cost.

Dechlorination using alkaline has the potential to remove chlorine both in raw water and CPO, but hydroxides (OH^-) can react with FFAs to form soap, which can unfortunately decrease the oil's quality. The presence of OH^- from common alkaline such as NaOH can be moderated in a liquid-liquid equilibrium by using sodium silicate (SS) that may behave like a buffer [9]. MPOB collaborates with us, in this regard, under a grant given by Ministry of Higher Education, Malaysia. Preliminary works of testing SS dilute solution in CPO were done, but no report was published due to inconsistent results. Issues with physical property of OH^- and NaOH dissociated from SS perhaps needs to be resolved. Therefore, the effect of the ratio between CPO and SS solution (SSS) on the OH^- concentration needs to be investigated and optimized to achieve the desired level of chlorine. This study aimed to investigate the effect of the ratio between crude palm oil (CPO) and SS solutions, and the SS concentration on the OH^- concentration in the various mixtures. The results of this study can provide valuable information for the CPO dechlorinating process and improve the quality of the final product.

2   EXPERIMENTAL METHODS

2.1 Materials

CPO was collected at Felda Lepar Hilir 3. The CPO sample was then filtered and stirred to ensure homogeneity. SS powder supplied by Bendosen was diluted in deionized water and distilled water to prepare its solution. Analytical grade of iso-propyl alcohol and hexane supplied by HmBG Chemical was used for gas chromatography GCMS analyses. Absolute ethanol from Fluka was applied in FTIR analysis for cleaning pH probe tips and pH buffer solutions of 4, 7, and 10 from Mettler Teledo were used in calibrating pH meter.

2.2 Experimental Design and Extraction Tests

CPO and SS solution were mixed at 40°C (equivalent temperature to clarifier in most mills) in the volume ratios that were varied based on One Factor at a Time (OFAT) in beakers. The beakers were attached with 1-mm scale graph paper to measure thickness of liquid layer as shown in Fig. 1. The volume ratios varied between 1:3 and 3:1, including replicates as suggested by Design Expert ver.7 software. The concentration of SS was 0.01 g/ml as proposed by Malaysian Palm Oil Board (MPOB) and the companies that applied SS in palm oil mills [10]. Mettler Teledo pH meter giving reading up to 2-decimal place was employed to measure pH after 12 h of mixing, from which hydroxide concentrations were calculated and the response variable. Table 1 shows the ratio of the liquids in continual, fractional values within 100 ml of total volume for 7 points including replicates.

Fig. 1. Heated, stirred beaker for reactive mixing and settling of SS and CPO

Table 1. Volume Ratios between CPO and SS solution

Run	Volume Ratio of CPO TO SS	CPO (ml)	SS (ml)
1	3.00	75	25
2	1.67	62.5	37.5
3	0.33	25	75
4	0.33	25	75
5	2.33	70	30
6	1.00	50	50
7	3.00	75	25

The experiment was then repeated by varying the concentration of SS solution from 0.0004 g/ml to 0.25 g/ml. The volume ratio of CPO:SS solution was kept constant at 7:3 because the others did not remain 2 clear liquid layers. Table 2 shows the concentration of the SS within 100 ml of total volume for 7 points including replicates.

Table 2: Concentration of SS Solution

Run	Concentration of SS (g/ml)
1	0.0626
2	0.1252
3	0.0004
4	0.2500
5	0.0004
6	0.1875
7	0.2500

2.3 Dissociation of Hydroxide from SS solution

Silica in low concentration of SS solution may pose acidic mixture due to bonding of silicon and oxygen at various structures [11]. The standard solutions of SS solution were prepared by using the half-serial dilution method [12] to avoid pipetting mistake. The dilution started with 0.01 g/ml of SS.

pH meter with 2-decimal point reading was preferably used to get immediate results. Other analysis methods, such as using titration would not get the actual hydroxide because of equilibrium shift during neutralization. The pH meter was calibrated by using three buffer solutions of different pH. Eq. (1) shows the dissociation of sodium silicate to form sodium hydroxide before OH$^-$ is formed in Eq. (2).

$$Na_2SiO_3 + H_2O \ \rightleftharpoons \ 2\,NaOH + SiO_2 \tag{1}$$

$$NaOH \rightarrow Na^+ + OH^- \tag{2}$$
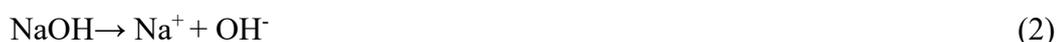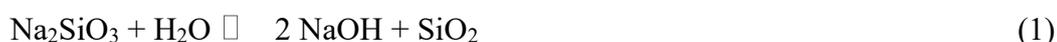
Hydroxide from SS was calculated via the equation of pH [13]

2.4 Profile of Crude Palm Oil by using GC-MS

Initially, CPO was filtered by using hydrophobic syringe filter made of PTFE in a 0.45-µm thickness and 25-mm diameter of a disc to separate suspended particle and aqueous solution. 1 mL of isopropyl alcohol or hexane solvent was mixed with 100 µL of the filtered CPO in vials by using micropipette. A gas chromatography, Agilent 6890 model, equipped with mass spectrometry detector (GC-MS) was used to analyze the analytes. The oven of the GC was mounted with SGE BPX5 column with the dimension of 30-meter length, 0.025-mm diameter and 0.25-µm film thickness. The oven temperature was raised from 40ºC at 10 ºC/min to 300ºC and remained at that temperature for 5 min.

2.5 Acid value determination by using auto-titrator.

Free fatty acid is normally formed during CPO storage [14] and periodical analysis was done to check its content. The procedure followed the acid value analysis standard namely MPOB Test Method c2.7:2004 which is also equivalent to AOCS Te a-64(1997)[15]. Free fatty acid problematically forms soap with NaOH and its quantity could be determined from the acid value analysis. 0.1 mol/L potassium hydroxide (KOH) solutions were prepared by dissolving KOH pellets in distilled water by using 1-L volumetric flask. The KOH solution was then used as a titrant to the auto-titrator from Metrohm, 785 DMP Titrino model. pH electrode LL Solvotrode (8.109.1586) Metrohm AG 9101 Herisau was used as the probe. The room temperature was set at 28 ºC. Initially, the system was calibrated with pH 7 buffer solution and the actual pH reading was set as the end point. The sample was prepared by diluting 5 ml of filtered CPO in 75 ml of isopropanol. The reading of pH and volume of KOH being used were recorded and analyzed. A blank test of isopropanol solvent was also included in the analysis. The titrations were repeated at least twice and the ceramic membrane of the pH probe was rinsed between the analysis runs by using absolute ethanol as this titration involved fatty liquid.

3 RESULTS AND DISCUSSION

Hydroxide ion is the key conjugate to sodium ion in NaOH that will be involved in the dechlorination reaction. The reaction was assumed to simultaneously occur when chloride was present in aqueous media or OH⁻ diffused to the organic phase of CPO, but the results will not be the focus in this report. Preliminary characterization of chemical and physical properties in perspective of extraction are presented here to further design the concept of dechlorination later.

3.1 Dissociation of Hydroxide from Sodium Silicate Solution

Information of pH on SS solution is necessary before its application to any liquid due to variety of silica structure from different suppliers and sensitivity of silicon to any presence of other ions, heat and light as a semiconductor element. Silica can form silicic acid in very dilute conditions. OH⁻ was determined from pH readings using Eq. (3)[16].

$$C_{OH^-} = \frac{1 \times 10^{-14}}{10^{-pH}} \tag{3}$$

Fig. 2 shows pH of SS solution at various concentrations. Two trends of data were captured by different models. By using the nonlinear regression in SigmaPlot 10, data was

fitted ($R^2 > 0.95$) with logarithmic Eq. (4) and quadratic Eq. (5) as respectively shown in Fig. 2(a) and (b).

$$pH = 13.8059 + 0.4218 \ln C_{SS} \tag{4}$$

$$pH = 6.99 - 157794.2C_{SS} + 2484503101.2C_{SS}^2 \tag{5}$$

where, C_{SS} denotes the concentration of SS solution in g ml^{-1}.
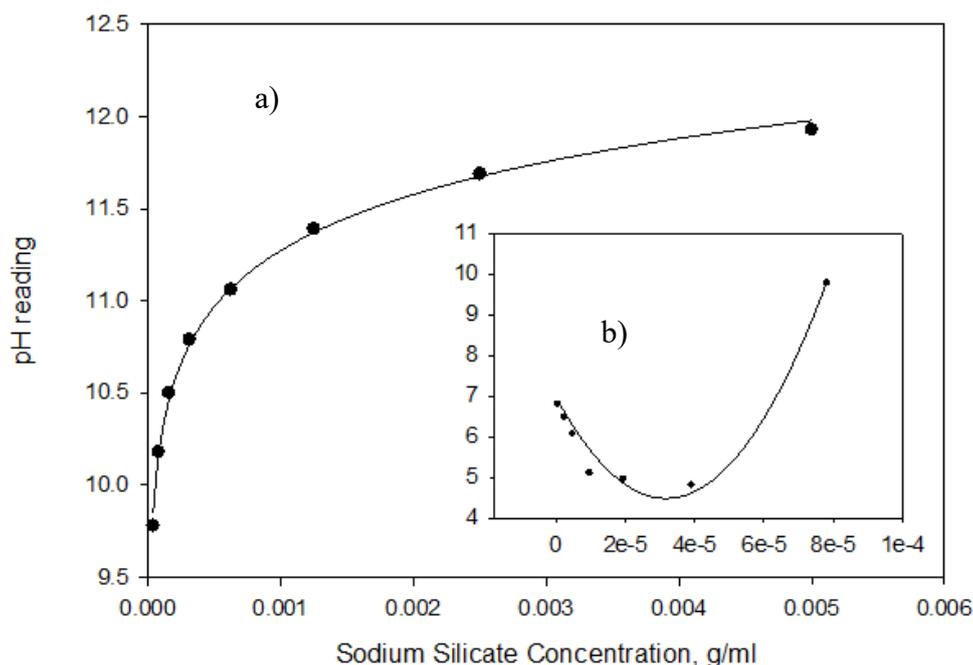
Fig. 2. pH at various SS concentrations

Based on the model, the logarithmic model of pH gives pH for 1 molar of SS 11 times lower than that of 1-M NaOH. This was probably the incomplete OH$^-$ dissociation from SS at an equilibrium at room temperature. A further analysis on molarity of SS and OH$^-$ revealed direct proportion in linear trendline from origin on their graph where its gradient is the dissociation constant of component, K_D, as shown in Eq. (6) at 28°C.

$$K_D = \frac{\left[OH^- \right]}{\left[Na_2SiO_3 \right]} = 0.0818 \tag{6}$$

The model of the plot is, however, valid until 6.344×10^{-5} g/ml because pH dropped below pH 7 and formed a curve as shown in the small graph in Fig. 2. Hence, acid condition clearly appeared below this concentration. The quadratic model that fitted it has a minimum pH 4.48 at 3.17×10^{-5} g/ml prior to a decrease until pH 7 when the concentration is 0. Perhaps, several form of silica structure created the acidic condition [9] in the form of silanol (Si-O-H) functional or silicic acid (SiO$_4^{4-}$) groups, thus silica falls under the category of acidic ligand, inorganic minerals and exhibits hydrophilic properties [17]. A comparison with pH of blank water indicated that about 10% difference in zero error of calibration revealed thus dissimilar standard reduction potential according to the Nernst Eq. for a pH measurement [18]. Therefore, the sample without SS would not be used as the reference in the calibration. Silica

from SS solution can be measured by using FTIR in the vibrational band in range between 1150 and 950 cm^{-1}. However, upon checking, its zero error was above 1% and this method is not practical for dilute SS solution.

3.2 Crude Palm Oil Profile and Free Fatty Acid Content

Analyses of chromatogram using mass spectroscopy detector were initially conducted by diluting CPO samples with isopropanol, the common solvent in AOCS titration analysis [19], but the GCMS analyte formed unclear layer of different density after a few minutes left on the autosampler rack. Result of replicates were not consistent with their original samples. Solubility of oil impurities might be the issue. Hence, hexane was used and able to minimize deviation of results with replicate analyses. Fig. 3 shows the chromatographic analysis result of CPO using hexane solvent in GCMS. Palmitic acid, or n-hexadecanoic acid had 40.20 % of fat at retention time of 17.975 min. Oleic acid and stearic acid or octadecanoic acids had 46.76 % and 9.62 %, respectively. These results were supported by Montoya, Cochard [20], which were close to 50 % of fat in palm oil was saturated, including 44% palmitic acid (C16:0), 5% stearic acid (C18:0), and traces of myristic acid (C14:0). About 40% of the fatty acids were unsaturated, including 10% polyunsaturated linoleic acid (C18:2) and linolenic acid (C18:3). Nonetheless, from the chromatogram analysis results, separation of FFA and conjugated fatty acids in glyceride was not possible using the SGE BPX5 column. Comparison between the fatty acid QUAL results and FFA content from acid value titration showed large differences. From the acid value test, FFA content of the sample used in the GCMS analysis was only 7.9 %. That sample was 7 days after collection. Initial collection, it was about 3%.
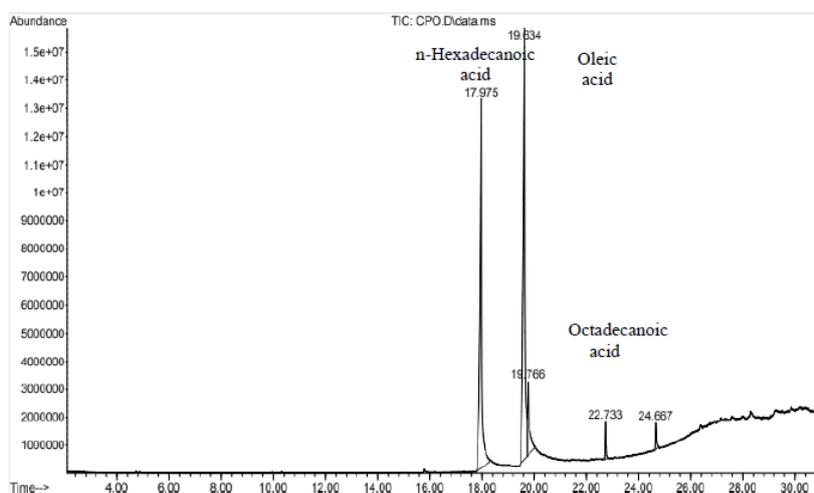

Fig. 3. Chromatogram of CPO Using GCMS

3.3 Effect of CPO-SS Volume Ratio

The pH reading decreased from 10.10 and plateaued out at 8.16 with the higher CPO volume. pH 8.16 was probably the value of buffering for SS in the mixture. The response of OH$^-$ concentration on various volume ratios of CPO and SS from 1:3 to 3:1 is shown in Fig. 4. The increase in the ratio decreased the hydroxide concentration, but no minimum at any pH was registered like the one previously resulted in the calibration curve at very low concentrations of SS probably due to the absence of acids from silica and free fatty acids (FFA). Pandey, Larroche [21] reported that pH of CPO was usually from 3.6 to 5.1, which is slightly acidic due to the presence of FFA from the hydrolysis of oil. In this study, the acid

value analysis revealed FFA content between 7.79 and 8 wt% in the CPO. Although this indicates that the oil samples degraded and its quality became off-spec for refinery process due to long storage in the experiment, pH remained above neutral with the presence of SS solution. The plot shows concave up decreasing shape.

One Factor Design (OFD) analysis was used to optimize the process and the correlation between concentration pH and the volume ratio is expressed in Eq. (7). This quadratic model was suggested among other polynomial models and parameters with the F value of 1.48 for Lack of Fit in Residual, indicating that this model significantly fitted the data.

$$[OH^-] = (11.94 + 11.4956\theta - 2.56373\,\theta^2)10^{-5}\text{mol/L} \tag{7}$$

Where, θ is volume ratio between CPO and SS. The above neutral and alkaline pH would not last. 7.41×10^{-5} mol/L, is the smallest concentration of OH^- could drop when CPO was more, Na_2O from SS was no longer available and hydrogen ion from acids or FFA became dominant, thus the buffering equilibrium had been breached.
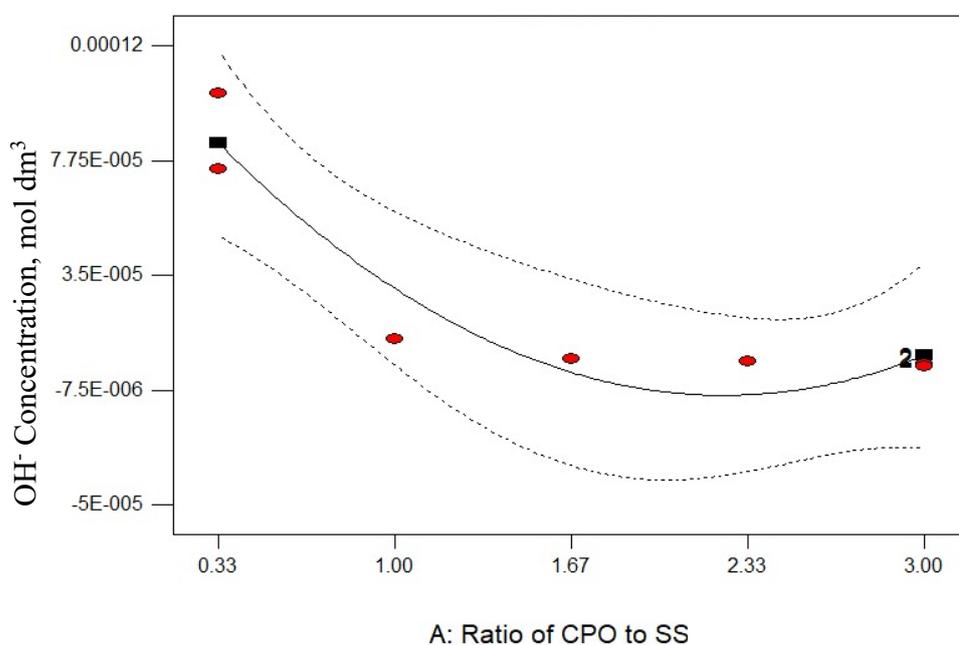

Fig. 4. The effect of volume ratio on hydroxide concentration.

Compared to OH^- dissociation from NaOH (or ionization), distribution constant of hydroxide from SS shown by Eq. (6) is relatively very low. Nevertheless, visibility of the second liquid phase was only evidenced at upper layer as shown in Fig. 1 from the CPO-SS volume ratio of 3:1 and 7:3. Table 2 shows the change of the volume ratio appeared after the mixture being settled for 12 h. The number of runs was not according to the sequence. The ratio dropped for about 67 to 78% from the original volume ratio due to the expansion of emulsion phase. This finding should be considered seriously if one intends to develop a liquid-liquid extraction as it will affect the liquid hold-up of the process. In this case, our painstaking experiment of hydroxide extraction as the key reactant for dechlorination in the aqueous phase will be started from 7:3 and above. The volume ratio below 0.33 can also be considered, since at that ratio, the liquid was bulkily emulsified so that clearer aqueous phase can hopefully be obtained and separated from the oil phase.

Table 2: Effect of Mixing to Volume

Run	Volume Ratio	Volume Ratio after 12 h
4	0.33	Single phase
3	0.33	Single phase
6	1.00	Single phase
2	1.67	Unclear layering
5	2.33	0.76
7	3.00	0.74
1	3.00	0.67

3.4 Effect of SS Concentration

Concentration of SS is another factor that will affect the presence of OH^-. In the OFAT analysis, pH increase was recorded as the concentration of SS increased, and the highest pH was 11.91 as shown in Fig. 5. However, no acidic condition was found. The quadratic model suggested by Design Expert was Eq. (8) and as shown in Fig. 5(a), could only fit 88.67% (R-squared) of the data while the regression using sigmoid model in Sigma Plot 10 as Eq. (9) in Fig. 5(b) could significantly fit 99.3%. Although the quadratic Eq. was best suggested, the fitness of the model was below 95% and insignificant.

$$\left[OH^-\right] = \left(1.878 + 4.01 C_{SS} + 2 C_{SS}^2\right) 10^{-3} \tag{8}$$

$$\left[OH^-\right] = \frac{0.0078}{1 + e^{\frac{0.1644 - C_{SS}}{0.0219}}} \tag{9}$$

Both models interestingly captured a downward curve, and the latter unveiled a trend that was symptomatic of autocatalysis. Dissociation of OH^- might be more than what was previously shown in the calibration curve. This also indicates that Na_2O was released more because of a reaction that consumed silicate, its conjugate in SS, started from 0.1644 g/ml, which is the middle point of the sigmoid graph. Because of undesired reactions other than dechlorination such as saponification and hydrolysis likely increase. This might justify why industries employed only 0.01 g/ml of SS solution in palm oil mills for oil extraction rate improvement.

3.5 McCabe Thiele Plot

Besides distillation column, McCabe Thiele method is also used to determine stages of mixer and settler for a solvent extraction process between two immiscible liquid phases. Fig. 6 shows two McCabe-Thiele plots for two volume ratios of CPO-SS from the results of volume ratio study above that remained two layers of liquid phase after 12 h of settling. Volume ratios of CPO:SS can be interpreted as operating lines on the McCabe-Thiele graphs, which were also symbolized θ. At θ = 3, the equilibrium was 3.62×10^{-8} and 1.13×10^{-6} g/g

of hydroxide in CPO and SS solution respectively. At θ = 2.33, both equilibria were from the same SS concentration, but they appeared at different points. This discrepancy might be due to different FFA content and other impurities that reacted with component of SS solution [22]. The equilibrium conditions of OH⁻ for both θs is all far below the operating lines, suggesting that at these volume ratios, hydroxide ion is not likely extractive to CPO [23].
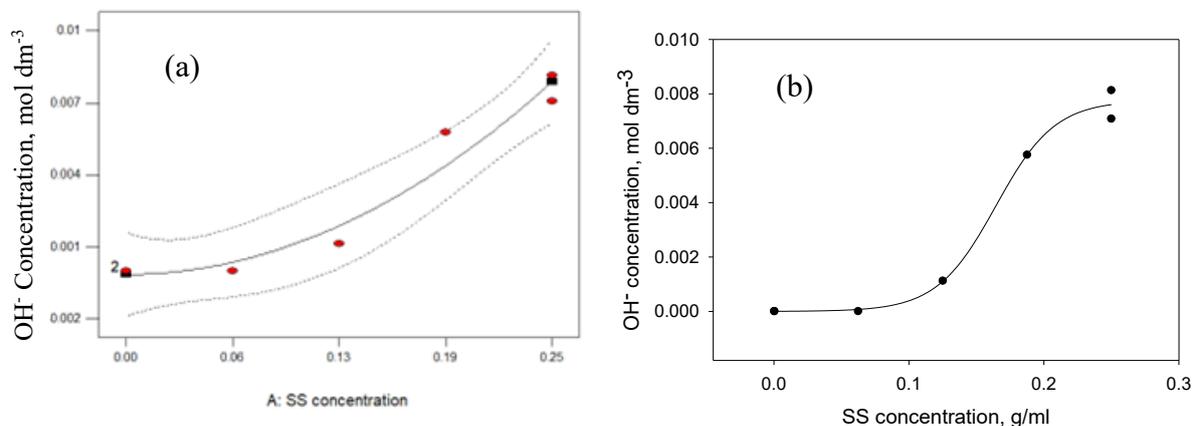

Fig. 5. The effect of SS concentration on hydroxide concentration for the volume ratio of 2.33.

The SS solution was 0.01 g/ml and OH⁻ from dissociated NaOH was not extracted to CPO. Thus, possibility of undesired hydrolysis reactions consuming free fatty acids and glycerides, which are highly non-polar and do not dissolve in the aqueous phase is low. In the case of SS concentration variation, clear 2-layer liquid formed at concentration of 0.0004 g/ml. Emulsion layer formed at 0.0625 g/ml and others concentration started from 0.1252 g/ml till 0.25 g/ml the second layer became solidified.
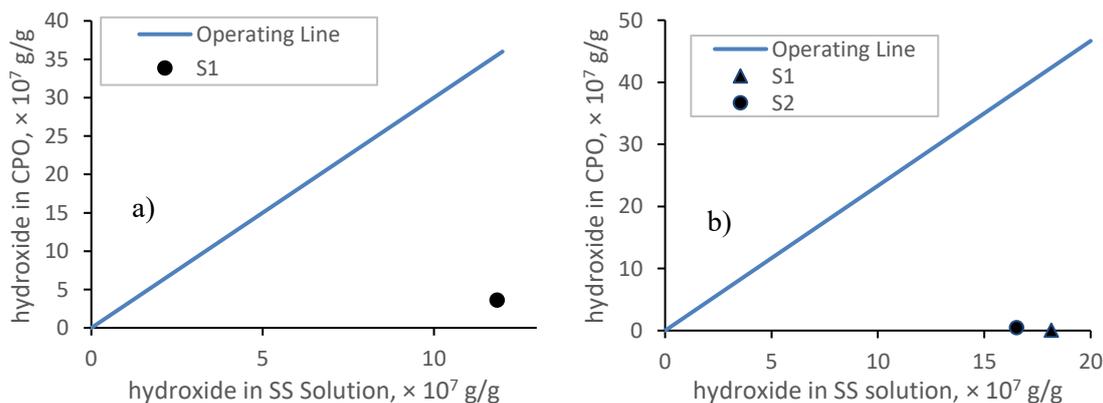

Fig. 6. McCabe-Thiele plot of solvent extraction for (a) θ = 3 and (b) θ = 2.33.

4   CONCLUSION

The effect of mixing CPO with SS solution at various volume ratios was investigated where hydroxide from NaOH that was dissociated from the SS solution was measured by using pH. The equilibrium condition for volume ratios of CPO:SS that secured biphasic condition were 7:3 and 3:1 and below the operating line according to McCabe-Thiele method, indicating that OH⁻ is not extractive. Only 0.004 g/ml concentration of SS formed 2 layers of liquid-liquid phase for OFAT varied concentration of SS. The acid values of the sample are

18.539 (mg KOH/ g CPO) and 18.982 (mg KOH/ g CPO), for sample 1 and sample 2, respectively. The free fatty acid contents in both samples are 7.79% and 8.01 %. OH^- concentration decreased following a quadratic model to the increase of volume ratios but it increased in a sigmoid model to the increase of SS concentration. The possible cause of these effects are detailed in the result discussion above.

ACKNOWLEGMENT

REFERENCES

[1]   Gao B, Li Y, Huang GYu L. (2019) Fatty Acid Esters of 3-Monochloropropanediol: A Review. Annual Review of Food Science and Technology. 10: 259-284. Available from: https://www.annualreviews.org/doi/abs/10.1146/annurev-food-032818-121245

[2]   Wei T, Liu W, Zheng Z, Chen Y, Shen MLi C. (2022) Bibliometric Analysis of Research Trends on 3-Monochloropropane-1,2-Diol Esters in Foods. Journal of Agricultural and Food Chemistry. 70: 15347-15359. Available from: https://doi.org/10.1021/acs.jafc.2c06067

[3]   Hilmi SMHS, Othman NH, Saparin N, Jahaya SS, Noor AMAsis AJ. (2019) Process for producing a refined palm fruit oil having a reduced 3-mcpd content. Available from: https://patents.google.com/patent/WO2019027315A2/en

[4]   Hassan NSM, Chew CLM, Tahir ZM, Amin Buhari Md Zain, Siran AJAM, Wok K, Yunus MFM, Jahaya SS, Rejab SAM, Mustaner MHilmi SMHS. (2019) An integrated oil extractor apparatus for sterilizing, digesting and pressing oil palm loose fruitlets. WO-2019216757-A1 Available from:
       https://patents.google.com/patent/WO2019216757A1/en?oq=WO-2019216757-A1

[5]   Nizam AFAMahmud MS. (2021) Food quality assurance of crude palm oil: a review on toxic ester feedstock. OCL. 28: 23-37. Available from: https://doi.org/10.1051/ocl/2021011

[6]   Chew CLSaparin N. (2021) Principal Formation and Mitigations Strategies for 3-MCPDE in Palm Oil Processing. Journal of Oil Palm and the Environment. 12: 86-95.

[7]   Oey SB, van der Fels-Klerx HJ, Fogliano Vvan Leeuwen SPJ. (2022) Chemical refining methods effectively mitigate 2-MCPD esters, 3-MCPD esters, and glycidyl esters formation in refined vegetable oils. Food Research International. 156: 111137. Available from: https://www.sciencedirect.com/science/article/pii/S0963996922001946

[8]   Kadir APG, Penguatkuasaan Tambahan Syarat Lesen yang Dikenakan bagi Pemegang Lesen dalam Kategori Kilang Buah Kelapa Sawit (MF), Kilang Penapis (RF), Pengeksport Keluaran Kelapa Sawit (PX) dan Pengimport Keluaran Kelapa Sawit (PM): Keselamatan Makanan dan Minyak Sawit yang Berkualiti, in (9)04/C/PD/656/4 Jil. 5, Berhad, M.P.O., Editor 2019, MPOB: Bangi, Selangor, Malaysia.

[9]   Bajpai P, (2014) 7 - Chemicals Used in Deinking and Their Function**Some excerpts taken from Bajpai, 2006 with kind permission from Pira International, UK, in Recycling and Deinking of Recovered Paper, Bajpai, P., Editor, Elsevier, Oxford; pp. 121-137. Available from: http://www.sciencedirect.com/science/article/pii/B9780124169982000076

[10] III DD, Zan HM, Hamid MFA, Idzhan NIMShukor MZ. (2017) Use of mineral salts to improve production of crude palm oil and controlling the oil lost. WO 2017/150965 Al: WO 2017/150965 Al

[11] Dankert Fvon Hänisch C. (2021) Siloxane Coordination Revisited: Si−O Bond Character, Reactivity and Magnificent Molecular Shapes. European Journal of Inorganic Chemistry. 2021: 2907-2927. Available from:
       https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/ejic.202100275

[12] Sapkota A. Serial Dilution- Definition, Formula, Calculator, Procedure, Uses. 2022 [cited 2023 12/5/2023]; Available from: https://microbenotes.com/serial-dilution/.

[13] Ryen Caenn HCHDaGRG (2017) Evaluating Drilling Fluid Performance,

[14] Ahmad Nizam AF, Muthiyah KMahmud MS. Free fatty acid formation in oil palm fruits during storage. in IOP Conference Series: Materials Science and Engineering. 2020. IOP Publishing, 991: 012009. Available from: https://dx.doi.org/10.1088/1757-899X/991/1/012009

[15] Yeong SK, Idris ZHassan HA, (2012) 20 - Palm Oleochemicals in Non-food Applications, in Palm Oil, Lai, O.-M., Tan, C.-P., and Akoh, C.C., Editors., AOCS Press; pp. 587-624. Available from: http://www.sciencedirect.com/science/article/pii/B978098189369350023X

[16] Ebbing DDGammon SD (2013) General Chemistry, Brroks/Cole Cengage Learning

[17] Singh S, Wasewar KLKansal SK, (2020) Low-cost adsorbents for removal of inorganic impurities from wastewater, in Inorganic Pollutants in Water, Devi, P., Singh, P., and Kansal, S.K., Editors., Elsevier; pp. 173-203. Available from: https://www.sciencedirect.com/science/article/pii/B978012818965800010X

[18] Shintani Y, Ogawa K, Saruya TKawarada H, Development of glassless all-solid-state pH sensor, Edition, Y.T.R.E., Editor 2017.

[19] Kuntom A, Lin SW, Ai TY, Idris NA, Yusof M, Sue TTIbrahim NA (2005) MPOB Test Methods, Malaysian Palm Oil Board

[20] Montoya C, Cochard B, Flori A, Cros D, Lopes R, Cuellar T, Espeout S, Syaputra I, Villeneuve P, Pina M, Ritter E, Leroy TBillotte N. (2014) Genetic Architecture of Palm Oil Fatty Acid Composition in Cultivated Oil Palm (Elaeis guineensis Jacq.) Compared to Its Wild Relative E. oleifera (H.B.K) Corte´ s.

[21] Pandey A, Larroche C, Dussap C-G, Gnansounou E, Khanal SKRicke S (2019) Biogas Production From Industrial Effluents, Elsevier, Academic Press

[22] Taifan GSPMaravelias CT. (2020) Integration of graphical approaches into optimization-based design of multistage liquid extraction. Computers & Chemical Engineering. 143: 107126. Available from:
https://www.sciencedirect.com/science/article/pii/S0098135420306256

[23] Barcelos TT, Martins M, Sousa RCoimbra JSdR. (2018) Liquid–Liquid Extraction of Neutral Lipids and Free Fatty Acids from Microalgae Oil. Journal of Chemical & Engineering Data. 63: 3391-3399. Available from: https://doi.org/10.1021/acs.jced.8b00281