Effect of Chemical Reactions on Unsaturated Content in Palm Oil

[1]Nur Aqilah binti Mohd Ali, and [2]Dr. Nurul Fadhilah binti Kamalul Aripin

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—The palm oil is originated from South Africa and widely use in various applications including producing glycoside from palm oil. However, the unsaturated content should remain same throughout the reduction process. Therefore, the unsaturated content can be determined using some method. There are three methods were employed in this study, one using wet experiment which is iodine titration to find iodine value (also known as Wijs method) and other two method is using analytical instrument which is Nuclear Magnetic Resonance (NMR) and Gas Chromatography-Mass Spectrometry (GCMS). For iodine titration, the iodine value for both palm oil and reduced palm oil was the same. For NMR, the unsaturated content can be determined based on oleic acid (also known as C18:1) peaks by looking at the peak integration. For GCMS, the unsaturated content can be determined based on oleic acid peaks in the GC chromatogram. In conclusion, the unsaturated content is not affected by the reduction process.**

Keywords— Unsaturated content, iodine value, palm oil, Wijs method, Gas Chromatography-Mass Spectrometry (GC-MS), Nuclear Magnetic Resonance (NMR) .

I. INTRODUCTION

Oil palm is a monocotyledon that can be obtained from species *Elaeis* and it has oil that contain 45% unsaturated content while the rest 55% is saturated content (Sambanthamurthi *et al.*, 2000). The oils can be useful towards various industry including glycoside, which is used to produce a new type of vesicle drug carrier (Aripin *et al.*, 2012). Therefore the palm oil need to undergo several steps of chemical reactions in order to produce glycoside from palm oil. Human body cannot produce unsaturated fatty acids since it is an essential fatty acids. This essential fatty acids (EFAs) was considered as functional foods and nutritional. Lot of research that was conducted has prove that these EFAs has significant roles in biological pathways which resulting in cardioprotective effect because of their potential to avoid serious diseases such as cardiovascular attack, cancer, osteoporosis, etc., (Orsavova *et al.*, 2015). The problem statement for this research studies unsaturation can easily affected through oxidation and other addition reactions which cause degradation to the compound.

Palm oil derived glycosides is useful in bio-related applications since it was categorized as biosurfactant. It called eco-friendly due to its biodegradable properties and low – toxicity. They were biodegradable due to its simple and complex structure (Otzen *et al.*, 2017).

Iodine value is measuring the degree of unsaturated content or double bonds in oil or fats other than to show the easiness of oils and fats oxidation (Tarmizi *et al.*, 2008). Unsaturated content can easily altered due to some factors such as exposure to light, air, moisture and high temperature. These factor can occur in the chemical reactions during the synthesis of glycosides (Shimamoto *et al.*, 2015). Therefore, monitoring through difference in iodine value is the best way to check the unsaturated content in every sample.

The aim of this studies is to determine the unsaturated composition of palm oil that undergoes glycosylation reaction through wet and analytical instrument which is Nuclear Magnetic Resonance and Gas Chromatography – Mass Spectrometry (GC-MS).

II. METHODOLOGY

A. Materials

The palm oil sample is obtained from processed palm oil (palm olein). Palm oil alcohol was produce from reduction process using $LiAH_4$ retrieved from the previous study using method from Aripin et al., using same palm oil sample (Aripin *et al.*, 2012). For iodine titration, solvent used was cyclohexane, glacial acetic acid, Wijs solution, potassium iodide, sodium thiosulphate solution and hexane and diethyl ether was purchased from Merck. For NMR analysis, solvent used was methanol-D4 was AR grade purchased from Sigma Aldrich. For GC-MS analysis, hexane and diethyl ether was AR grade purchased from MERCK.

B. Wijs method (Iodine titration)

Sample is weighed about 0.05g and dissolved in 3.75 mL of solvent mixture (prepared by mixing equal volume of cyclohexane and glacial acetic acid and 8 mL of 0.1 M Wijs solution. The solution was kept in dark for an hour to allow it to rest. A blank is prepared in the same manner but did not contain any samples. Then, 7 mL of 10g/100mL potassium iodide solution was added using pipette and add it to the solution contained sample and blank. Titration with standardized 0.1 mol L-1 sodium thiosulfate solution using a 50 mL digital manual burette was carried out until the solution was a pale yellow color. The iodine value was given by equation 1 below:

$$IV = \frac{12.69\ C\ (V_1 - V_2)}{m} \qquad \text{(Equation 1)}$$

where C is the exact concentration (mol L^{-1}) of the standard sodium thiosulfate solution; V1 is the volume (mL) of standard sodium thiosulfate solution used for blank test; V2 is the volume (mL) of standard sodium thiosulfate solution used for sample titration; and m is the mass (g) of the oil sample.

C. NMR preparation

The samples were characterized by ^{1}H-NMR using d-chloroform. Measurements were conducted at room temperature. All proton spectra were measured on a JEOL NMR spectrometer at 400 MHz.

D. GC-MS preparation

Samples were quantified by gas chromatography using the 450 GC/220 MS system (Varian. Inc, USA) and 5975C inert MSD with triple-Axis detector (Agilent Technology, USA). HP-5ms was used as column in GC/MS (5%-diphenyl, 95%-dimethylpolysiloxane, 30 m x 0.250 mm ID x 0.25 µm). The temperature program was set up from 50 °C to 250 °C with 5°C/min, both the injector and detector temperatures were 280 °C, and helium was used as carrier gas. The injection volume was 2µL.

III. RESULTS AND DISCUSSION

A. Wijs Method : Iodine Value

The standard range of iodine value for palm oil is 50.6 to 55. Table 1.0 below shows the average of data for two times repetitions.

Table 1.0 *Titration data*

Sample	Iodine value	Consistency
Blank	11.9 ± 0.2	-
PO	53.9 ± 0.3	0.5 %
PO-OH	52.8 ± 2	3.3 %

Based on Table 1.0, the obtained iodine value for every sample is quite consistent to which the standard deviation value is below 5%. The unsaturated content of palm oil is similar to the reduced palm oil showing that the reduction process does not affect the unsaturated content the unsaturated content. The iodine value obtained from this experiment is quite similar to iodine value of palm oil at room temperature which is 52.62 (Tarmizi *et al.*, 2008).

B. Nuclear Magnetic Resonance

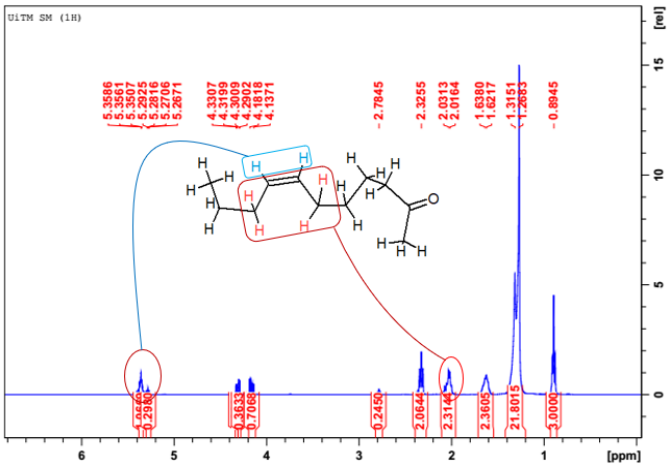

Fig. 1.1*: ^{1}H-NMR spectrum of palm oil.*

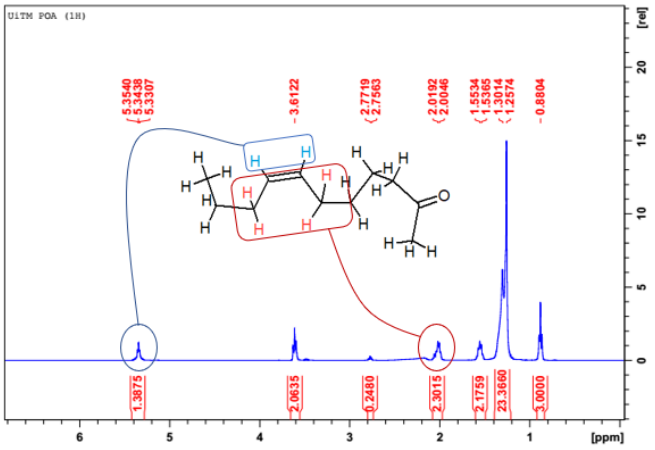

Fig. 1.2*: ^{1}H-NMR spectrum of palm oil alcohol (after reduction).*

The spectrum of palm oil alcohol and palm oil alcohol was shown in Figure 1.1 and Figure 1.2 respectively. The presence of peak at 3.6 ppm, confirms that the conversion of ester to alcohol and the absence of ester peak at 2.2 ppm strengthen the confirmation.

The unsaturated content is observed by looking at peak 2.03 ppm and peak 2.02 ppm in Figure 1.1 and Figure 1.2 respectively. Both spectrum showed 58% unsaturated content which is calculated from the peak integrations. However, this value is slightly higher than the reported value which may be caused by improper peak integration caused by the spectrum baseline.

C. Gas Chromatography – Mass Spectrometry (GC-MS)

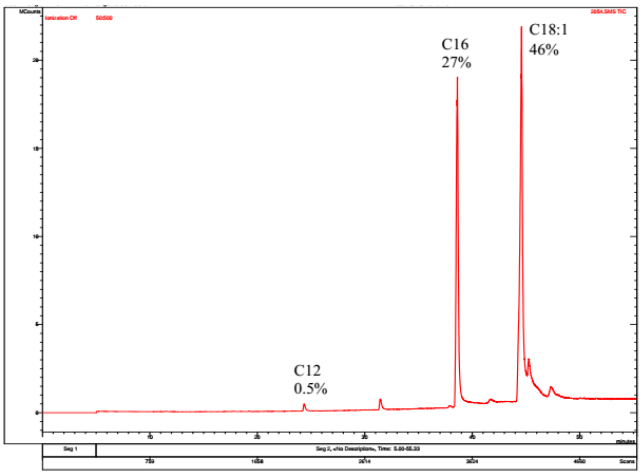

Fig. 1.3*:Chromatogram plot of palm oil alcohol*

From the GC chromatogram The unsaturated content can be determined based on C18:1 (oleic acid) peak at 44 ppm. It is determined that the unsaturated compounds content is around 46%. This value is more consistent with the reported values compared to the NMR result. However, we could not compare the unsaturated content in palm oil alcohol with palm oil because of the incomplete measurement of palm oil sample. The palm oil sample requires remeasurement but due to time constraint, it could not be done. Therefore, in order to improve this result, the sample should be

analyzed multiple times in order to obtain most optimum result (Ronderos-Lara *et al.*, 2018).

IV. Conclusion

We conclude that there is unsaturated content in both palm oil and palm oil alcohol are not affected by the reduction process. Analyses using NMR, GC-MS and IV determination confirmed the result.

Acknowledgment

I would like to express my gratitude toward Dr. Nurul Fadhilah for helping in my research project and also towards Universiti Teknologi Mara for provide facilities and equipment to finish this study.

References

[1] Aripin, N. F. K.*, et al.* (2012). Preparation of vesicle drug carrier from palm oil- and palm kernel oil-based glycosides. *Colloids and Surfaces B: Biointerfaces*(95), 144–153. doi:10.1016/j.colsurfb.2012.02.032

[2] Orsavova, J.*, et al.* (2015). Fatty Acids Composition of Vegetable Oils and Its Contribution to Dietary Energy Intake and Dependence of Cardiovascular Mortality on Dietary Intake of Fatty Acids. *Int J Mol Sci, 16*(6), 12871-12890. doi:10.3390/ijms160612871

[3] Otzen*, et al.* (2017). Biosurfactants and surfactants interacting with membranes and proteins: Same but different? *Biochim Biophys Acta Biomembr, 4*, 639-649.

[4] Ronderos-Lara, J.*, et al.* (2018). Optimization and Application of a GC-MS Method for the Determination of Endocrine Disruptor Compounds in Natural Water. *Separations, 5*(2). doi:10.3390/separations5020033

[5] Sambanthamurthi, R.*, et al.* (2000). Chemistry and Biochemistry of Palm Oil. *Palm Oil Research Institute of Malaysia*.

[6] Shimamoto, G. G.*, et al.* (2015). Simple Methods via Mid-IR or1H NMR Spectroscopy for the Determination of the Iodine Value of Vegetable Oils. *Journal of Brazilian Chemical Society, 26*(7), 1431-1437. doi:10.5935/0103-5053.20150111

[7] Tarmizi, A. H. A.*, et al.* (2008). Palm-Based Standard Reference Materials for Iodine Value and Slip Melting Point. *Analytical Chemistry Insights, 3*, 127–133.